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Baseline Scotland: groundwater chemistry of the Carboniferous sedimentary aquifers of the Midland Valley

Groundwater Programme

Open Report OR/11/021

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Keywords

Baseline, groundwater, chemistry, Scotland, Carboniferous.

Front cover

Sampling a pumped outflow from an abandoned coal mine in East Lothian.

Bibliographical reference

Ó DOCHARTAIGH B É, SMEDLEY P L, MACDONALD A M, DARLING W G AND HOMONCIK S. 2011. Baseline Scotland: groundwater chemistry of the Carboniferous sedimentary aquifers of the Midland Valley. *British Geological Survey Open Report*, OR/11/021. 105pp.

Keyworth, Nottingham British Geological Survey 2011

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Foreword

Groundwater in its natural state is generally of excellent quality and an essential natural resource for Scotland. Groundwater directly accounts for at least 7% of public water supply, as well as sustaining river flows and water to some 30 000 private supplies. However, the natural quality of groundwater in our aquifers is continually being modified by the influence of man. This occurs due to direct and indirect anthropogenic inputs and to groundwater abstraction. Therefore, a thorough knowledge of the quantity and quality of groundwater in our aquifers, including an understanding of the processes that affect groundwater, is essential for effective management of this valuable resource.

Baseline Scotland, jointly conceived and funded by BGS and SEPA, seeks to improve the data availability and general understanding of the chemistry of Scotland's groundwater. The primary aim of the project is to provide core hydrogeological data and interpretation to help in the implementation of the Water Framework Directive. An overview of groundwater chemistry data for Scotland during the inception phase (MacDonald and Ó Dochartaigh 2005) highlighted the paucity of reliable data for natural substances that occur in groundwater. Good-quality data that do exist are available for only small areas, e.g. the Dumfries aquifer – but the Water Framework Directive requires an understanding of background levels across a much broader area.

The aims of *Baseline Scotland* are:

1. To characterise the ranges in natural background groundwater quality in the main aquifer types in Scotland, by carrying out groundwater sampling surveys that as far as possible incorporate representative areas of each aquifer, allowing extrapolation of the interpreted results to the remaining parts of each aquifer.

2. To provide a scientific foundation to underpin Scottish, UK and European water quality guideline policy, notably the Water Framework Directive, with an emphasis on the protection and sustainable development of high quality groundwater.

The project runs from 2005 to 2011, during which time systematic surveys will be undertaken across the different aquifers of Scotland. As we move forward, Scotland will be in a much better position to develop and manage its groundwater resources.

Alan MacDonald BGS

Vincent Fitzsimons SEPA

Acknowledgements

The authors would like to acknowledge the help of a number of BGS and external colleagues during the course of this project:

Debbie Allen, BGS

Paul Butler, SEPA

Vincent Fitzsimons, SEPA

David Goold, Composite Energy

Charlie Gowing, BGS

Naomi Le Feuvre, SEPA

Chris Milne, BGS

Ian Watson, Coal Authority

We would also like to thank the owners of all the groundwater sources sampled for this project for their time and assistance in the field.

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Summary

This report describes the baseline groundwater chemistry of the sedimentary aquifers of Carboniferous age in the Midland Valley of Scotland. Groundwater is an important resource in the Midland Valley, largely for agriculture, but also for industry – including food and drink processing and mineral water bottling, and for domestic use. A large but unquantified volume of groundwater is also still pumped from former mine workings, largely coal mines, in order to maintain water levels and for quality treatment.

Analyses for 62 groundwater samples were interpreted for the purposes of this study. Of these, 36 samples were collected for the Baseline Scotland project between September and December 2008. These were augmented with a further 25 samples collected during separate BGS projects since 2001. The sites were chosen largely to be representative of groundwater in the area, and sources that were very poorly constructed were avoided. A small number of samples were deliberately targeted from mines, either from adits, shafts or boreholes. The data were classed in one of five different hydrogeological units (or aquifer groups): four chronostratigraphic groups, which in decreasing order of age are the Inverclyde, Strathclyde, Clackmannan and Coal Measures groups; and a fifth group incorporating waters sampled from mine discharges.

An estimate of the baseline groundwater chemistry conditions in the four chronostratigraphic hydrogeological units is presented, based on a statistical summary of the chemical data, which represents values between the 10^{th} and 90^{th} percentiles of the full dataset range. This statistical approach to estimating baseline compositions was complemented by selecting 11 analyses of groundwater from sources where there is little or no indication of direct contamination, including likely impact from mining. The chemistry of these samples represents the typical groundwater conditions in the four non-mine hydrogeological units in the sedimentary Carboniferous aquifers of the Midland Valley.

A summary of the conclusions arising from this study follows.

Groundwater flow

1. Many of the groundwater samples are from deep boreholes, where groundwater is often present under confined conditions and within multilayered aquifers. Groundwater movement is dominated by flow within fractures. Analysis of dissolved gases and stable isotopes indicates that groundwaters contain a high proportion of relatively old water, recharged more than 35 years ago, with a significant proportion of water recharged more than 60 years ago. However, there is no evidence of the existence of palaeowater (older than 10,000 years).

2. Many of the groundwaters show evidence of having been impacted by ion-exchange reactions (Na for Ca exchange), which suggests that young shallow groundwater has mixed with older, more mineralised water.

Baseline chemistry

3. The groundwaters show a very wide range of solute concentrations, with a 10^{th}–90^{th} percentile range for TDS (total dissolved solids) of 274 to 1620 mg/L, and a median of 555 mg/L. The lowest TDS value was from groundwater from a spring, which also had the lowest alkalinity. The highest was in reducing groundwater from a deep borehole (>1000 m) in the Coal Measures Group. There are some distinct differences in groundwater chemistry between the aquifer groups. The most mineralised groundwaters (excluding mine discharges) are from the Coal Measures Group, which also have the lowest dissolved oxygen (DO) concentrations. At least some of the groundwaters identified as being from the Coal Measures Group are likely to have been impacted in some way by coal mining. The least mineralised groundwaters were from the Inverclyde and Strathclyde groups.

4. Groundwater pH is usually near-neutral, with a 10^{th}–90^{th} percentile range of 6.40 to 7.84. There is little apparent difference in pH between the different aquifer groups. The pH data indicate that the acid-buffering capacity of the aquifers is high (even for mine discharges), most probably controlled by dissolution of carbonate minerals. Alkalinity is variable but often high, with a 10^{th}–90^{th} percentile range of 132 to 510 mg/L. The main species contributing to groundwater alkalinity is HCO_3. The highest median alkalinity values are in the Coal Measures Group, although some high concentrations also occur in the Clackmannan Group.

5. Many of the groundwaters sampled were reducing (anoxic), with 37% of determined dissolved oxygen concentrations less than or equal to 1 mg/L and 60% of determined Eh values less than 250 mV. Groundwaters from the Clackmannan Group and Coal Measures groups are the most reducing (excluding the mine discharges). Field sampling showed evidence (by smell) that some of the groundwater sources from the Clackmannan and Coal Measures groups contained dissolved sulphide, indicating the presence of strongly reducing conditions in some parts of these aquifers. Detectable dissolved methane was measured in a number of the samples. Samples from the Strathclyde and Inverclyde groups show the highest dissolved oxygen concentrations. High concentrations of dissolved organic carbon (DOC) (up to 70.8 mg/L) in a few samples are also indicative of the reducing – often strongly reducing – nature of some of the groundwaters.

6. Groundwater types encompass a large range from Ca-HCO_3, through Ca-Mg-HCO_3, SO_4-rich types, Na-HCO_3, and (rarely) Na-Cl. The groundwaters have variable calcite saturation indices but in many cases are close to saturation, indicating both the presence of, and reaction with, carbonate minerals in the aquifers.

7. There is a wide range in concentrations of the major anions. Concentrations of Cl are typically high, but the 10th percentile is 7.2 mg/L and the 90th percentile is 123 mg/L. The highest value (11,500 mg/L) is from a very deep (>1000m) borehole. Concentrations of SO_4 span some five orders of magnitude, with a 10^{th}–90^{th} percentile range of 4.7–179 mg/L. The overwhelmingly dominant processes controlling this large range are likely to be oxidation of sulphide minerals, particularly in mining-impacted waters; and sulphate reduction in the most reducing conditions. Low concentrations (<5 mg/L SO_4) are usually associated with low NO_3-N concentrations and often high NH_4-N; all samples recorded in the field as having a smell of H_2S had SO_4 concentrations <5 mg/L.

8. There is large spatial variability in concentrations of the major cations. The highest concentrations of Ca and Mg are in mine waters and some Coal Measures Group groundwater, probably due to reaction of carbonate minerals and clays, which could have been enhanced by the generation of acid during the oxidation of iron sulphide. Concentrations of Na are also often high, particularly in groundwaters from the Coal Measures and Clackmannan groups and mine waters. Concentrations of K are also correspondingly high. The high concentrations of dissolved cations are likely to reflect the effects of extreme water-rock interaction, in some cases (particularly deep boreholes) involving long residence times in the aquifers concerned. Sodium is probably largely sourced from dissolution of silicate minerals and ion-exchange reactions, the latter induced by young shallow groundwater mixing with older saline water.

9. Concentrations of Fe and Mn show large ranges, consistent with the large variations in redox status of the aquifers. The highest Fe and Mn concentrations are in groundwater from the Coal Measures Group and Clackmannan Group. Both elements are found at highest concentrations in groundwaters with low dissolved oxygen concentrations.

Nitrate and phosphate

10. The distribution and large variations in NO_3-N concentrations also show the strong control that redox has on groundwater chemistry, indicating that denitrification – which occurs under reducing conditions – has been important in many of the groundwaters. Nitrite is detectable in a few low NO_3 groundwaters and, as an intermediate reaction product, is an additional indication of denitrification. Concentrations of NH_4-N are high in a number of samples, in several exceeding 1 mg/L, and are consistent with reaction of natural organic matter in the aquifers. The distribution of N species supports evidence from other redox-sensitive parameters that groundwaters from the Coal Measures Group and mine discharges are the most strongly reducing.

11. The highest P concentrations are in the Coal Measures and Clackmannan groups, with sources likely to include dissolution of phosphate minerals, desorption from iron oxides under reducing conditions and degradation of organic matter. Agricultural pollution may be contributory in some cases, but some of the outlier P concentrations occur in the more reducing (and mine-impacted) groundwaters. This is consistent with a natural origin.

Dissolved gases

12. Dissolved carbon dioxide (CO_2) was measured on selected groundwaters and the results indicate that pCO_2 is often high, controlling carbonate equilibrium. Dissolved methane (CH_4) was present at 10 µg/L or less in approximately half the samples measured. Such values are typical of those found in major UK aquifers such as Cretaceous Chalk and the Permo-Triassic Sherwood Sandstone Group. The remainder of the samples range up to *ca.* 10 mg/L. Waters with dissolved CH_4 concentrations higher than 1.5 mg/L can, in principle, give rise to explosive atmospheres in confined situations such as buildings and excavations.

Mining

13. Mining activity has had a major impact on groundwater quality in the region. This is particularly the case for the samples collected directly from discharges (pumped or gravity flows) from abandoned coal mines. The mine discharges are particularly mineralised, with high SEC values and particularly high concentrations of HCO_3, Ca, SO_4, Fe and Mn. The waters are generally low in dissolved oxygen and show evidence of pyrite oxidation within the mined areas. The pH values are generally well-buffered and alkalinity is high, indicating significant reaction with carbonate minerals in the aquifers. Similar groundwater chemistry is seen in some other groundwaters from the Midland Valley, particularly from the Coal Measures and Clackmannan Groups, which were collected from boreholes or shafts that, while not specifically abstracting mine waters, are suspected to intercept abandoned mine workings. Mine waters may therefore impact areas away from obvious sources of mine discharge.

1 Introduction

This report describes the baseline groundwater chemistry of the Carboniferous sedimentary aquifers of the Midland Valley, Scotland (Figure 1). This region lies between the Highland Boundary Fault to the north and the Southern Upland Fault to the south, and is also often termed the Central Belt of Scotland. It is the most densely populated part of Scotland, containing the two largest cities, Glasgow and Edinburgh.

The northern parts of the Midland Valley, in the Vale of Strathmore and central Fife, are predominantly underlain by Devonian sedimentary and volcanic rocks. The baseline chemistry of the Lower Devonian sedimentary aquifer in much of Strathmore was addressed in an earlier report in this series (Ó Dochartaigh et al. 2006). The remaining Devonian aquifers in the northern Midland Valley, and the Permian basin aquifer at Mauchline, will likewise be reported on separately. This current report addresses the Carboniferous sedimentary aquifers which dominate the central and southern parts of the Midland Valley, to the south of a line that runs roughly from Greenock in the west through Stirling to the coast at St Andrews in Fife (Figure 1).

These Carboniferous sedimentary rocks underpinned much of the industrial prosperity of Scotland from the late 18th to the mid 20th centuries. Mineral resources, in particular coal, oil shale and ironstone, were intensively exploited to support industrial and economic development. Carboniferous sandstone was also extensively quarried for high-quality building stone. The last deep coal mine in Scotland, Longannet in west Fife, closed in 2002, but coal is still worked by open-cast mining at sites across the Midland Valley. The legacy of mining has a major impact on the hydrogeology and hydrochemistry of the Carboniferous aquifers.

Historically, Carboniferous aquifers in the Midland Valley were more intensively used for groundwater supplies than any other in Scotland, particularly for industrial activities. Today, the volume of groundwater abstracted in the area is much less, and is predominantly used for agriculture, although considerable volumes (probably more than 50 Ml/d) are abstracted from abandoned mines to manage groundwater levels and poor groundwater quality.

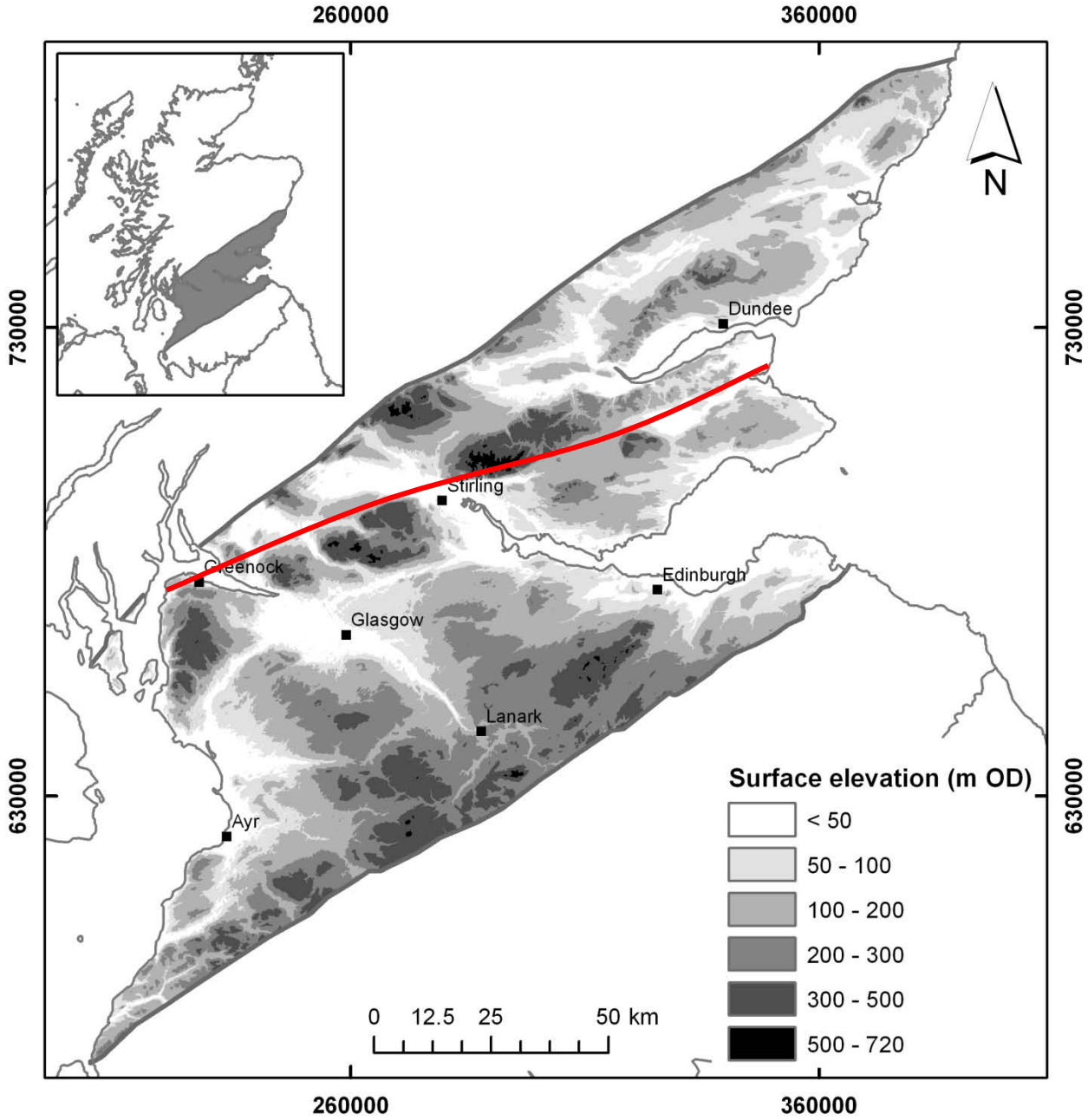


Figure 1 The Midland Valley of Scotland, showing land surface elevation; bounded to north and south by major regional faults. The red line marks the approximate northern boundary of the study area (the northern limit of the outcrop of Carboniferous sedimentary rocks).

2 Background

In order to understand the chemistry of the groundwater in the area, it is important to understand the environmental context. This chapter sets out the geology, land use and hydrogeology of the area to provide a physical framework for the groundwater system, and also discusses available rainfall chemistry data to help define the initial chemical composition of groundwater recharge.

2.1 LAND USE

The most urbanised parts of Scotland are concentrated within the Midland Valley, with extensive urban districts extending from Ayrshire to Edinburgh. It is the industrial heartland of Scotland, once the focus of industries from extractive mining and quarrying, to heavy manufacturing such as the iron and steel and shipbuilding industries, and a range of food and drink production mainly related to brewing and distilling. Although heavy industry has declined in recent decades, the Midland Valley still remains the main focus of manufacturing, which is now typically lighter, including pharmaceuticals, food and drink. Ayrshire and the wider Glasgow area still retain many industrial areas.

Away from urban areas, agriculture is an important activity. Arable agriculture dominates in the east, particularly in East Lothian and Fife: largely wheat, vegetables and fruit. Sheep and dairy farming dominate in the south and west: sheep farming particularly in the more upland areas, and dairy farming in Ayrshire (MLURI 1993; Figure 2).

The highest ground, largely underlain by Carboniferous volcanic rocks, is largely moorland with low intensity agriculture and some commercial forestry (Figure 2). Recently, wind farms have been developed in some of these areas.

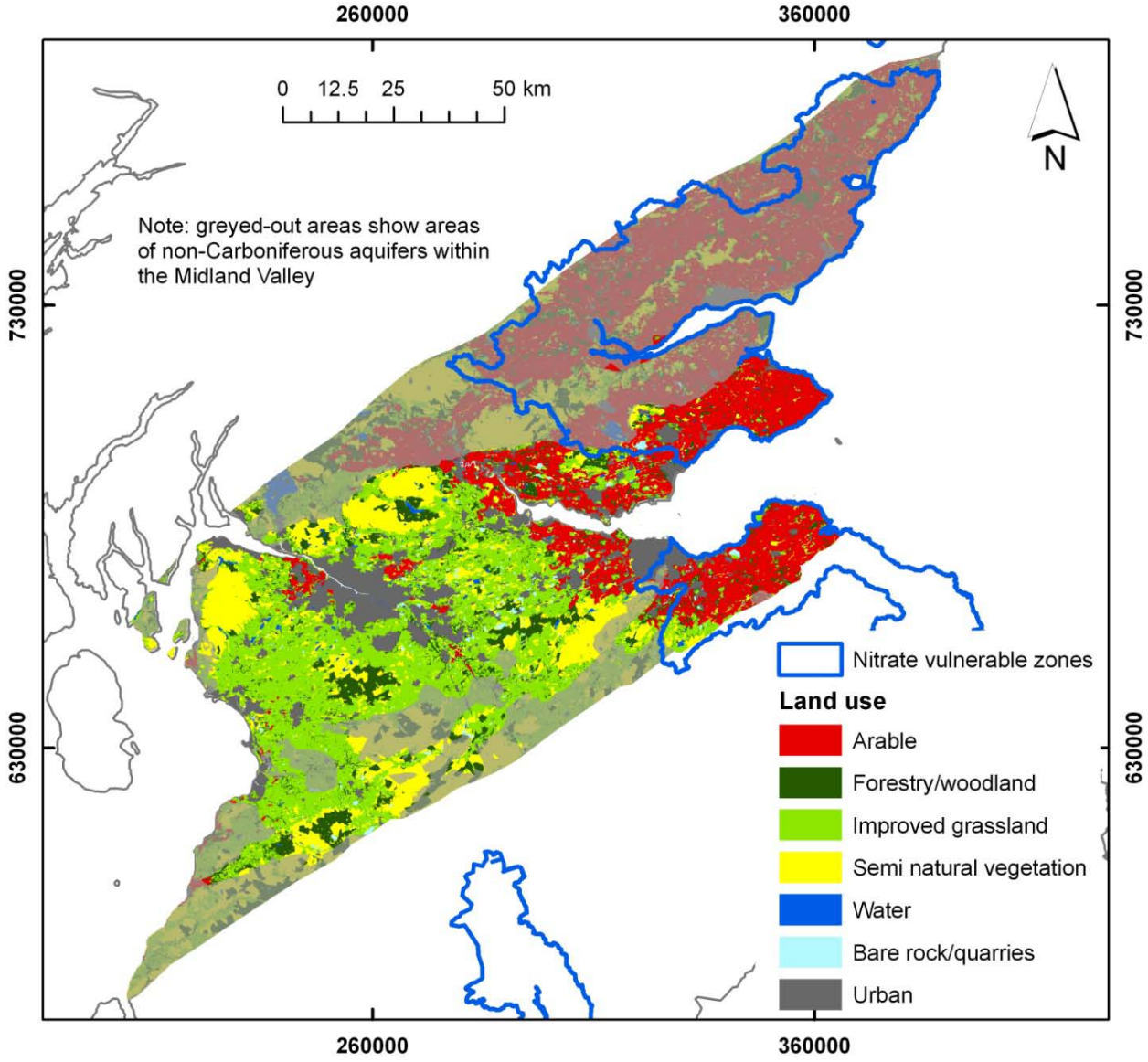


Figure 2 Generalised land use in the Midland Valley, with nitrate vulnerable zones highlighted. The areas outwith the current study are partially greyed out.

2.2 BEDROCK GEOLOGY

The Midland Valley comprises a graben bounded to the north by the Highland Boundary Fault and to the south by the Southern Upland Fault (Figure 3). It contains the most extensive sequence of Carboniferous rocks preserved in Scotland. The northern parts of the Midland Valley, in the Vale of Strathmore north of Dundee, and in central Fife, are predominantly underlain by Devonian sedimentary and volcanic rocks, which are discussed in a separate report (Ó Dochartaigh et al. 2006).

Throughout the Carboniferous period, erosion of mountains to the north and south supplied sediment into the Midland Valley graben. The earlier sedimentary successions, dating from the Tournaisian and Visean stages, are the **Inverclyde** and **Strathclyde groups**, which crop out largely along the northern and southern boundaries of the study area, as well as the area between Edinburgh, Linlithgow and Lanark. Small outcrops of Inverclyde Group rocks are recognised on the north and south banks of the Tay estuary, representing the most northerly outliers of Carboniferous rocks. These represent a mosaic of fluvial, fluviodeltaic and lacustrine-lagoonal environments in semi-isolated basins that often show quite different stratigraphies. The climate in the Tournaisian was semi-arid, with markedly seasonal rainfall, which resulted in the

formation of cornstones (pedogenic calcretes) in some Inverclyde Group sandstones. Later, in the Visean, as Scotland moved nearer the equator, the climate became progressively wetter, supporting the growth of swampy forests which gave rise to coals that are seen in the Strathclyde Group (Read et al. 2002). The main subdivisions in the Inverclyde Group are the Kinnesswood and Ballagan formations. In the Strathclyde Group different sedimentary formations are named in Fife, West and East Lothian, due to the difficulty in correlating between separate basins.

During the early Carboniferous period, extensive rift-induced basaltic volcanism, associated with the formation of the Midland Valley graben, produced thick sequences of volcanic rocks. The most extensive is the Clyde Plateau Volcanic Formation, which crops out in the north-central and western parts of the Midland Valley forming the Renfrewshire hills, Campsie and Kilpatrick hills (Figure 3). Less extensive units occur across the region, particularly in East Lothian where the Garleton Hills Volcanic Formation crops out, with smaller outcrops in Fife, Edinburgh, West Lothian, Lanarkshire and south Kintyre (Read et al. 2002).

At the top of the Strathclyde Group, the Hurlet Limestone marks a widespread marine transgression which progressively led to the submergence of most of the upstanding volcanic piles, and a much more uniform, marine and shallow marine influenced environment across the Midland Valley. Much of the resultant **Clackmannan Group**, which generally crops out closer to the centre of the basin than the Inverclyde and Strathclyde groups, comprises a series of cyclical marine and fluviodeltaic sedimentary rocks. These are the Upper and Lower Limestone formations and the intervening Limestone Coal Formation, which change to more proximal, dominantly fluvial rocks in the Passage Formation at the top of the group (Read et al. 2002).

The uppermost rocks in the Carboniferous are the **Coal Measures**, divided into Lower, Middle and Upper Coal Measures. These are dominant in Ayrshire in the west and the Glasgow-Falkirk-Alloa area in the centre of the Midland Valley. There are two smaller outcrops at Glenrothes in Fife and east of Edinburgh. The Coal Measures are generally fluviodeltaic in origin, with some marine incursions, passing upwards into terrestrial ‘red beds’, which are barren of coal, at the top of the sequence (Read et al. 2002).

The total thickness of Carboniferous rocks across the Midland Valley varies but in most places is 2000–3000 m (Read et al. 2002).

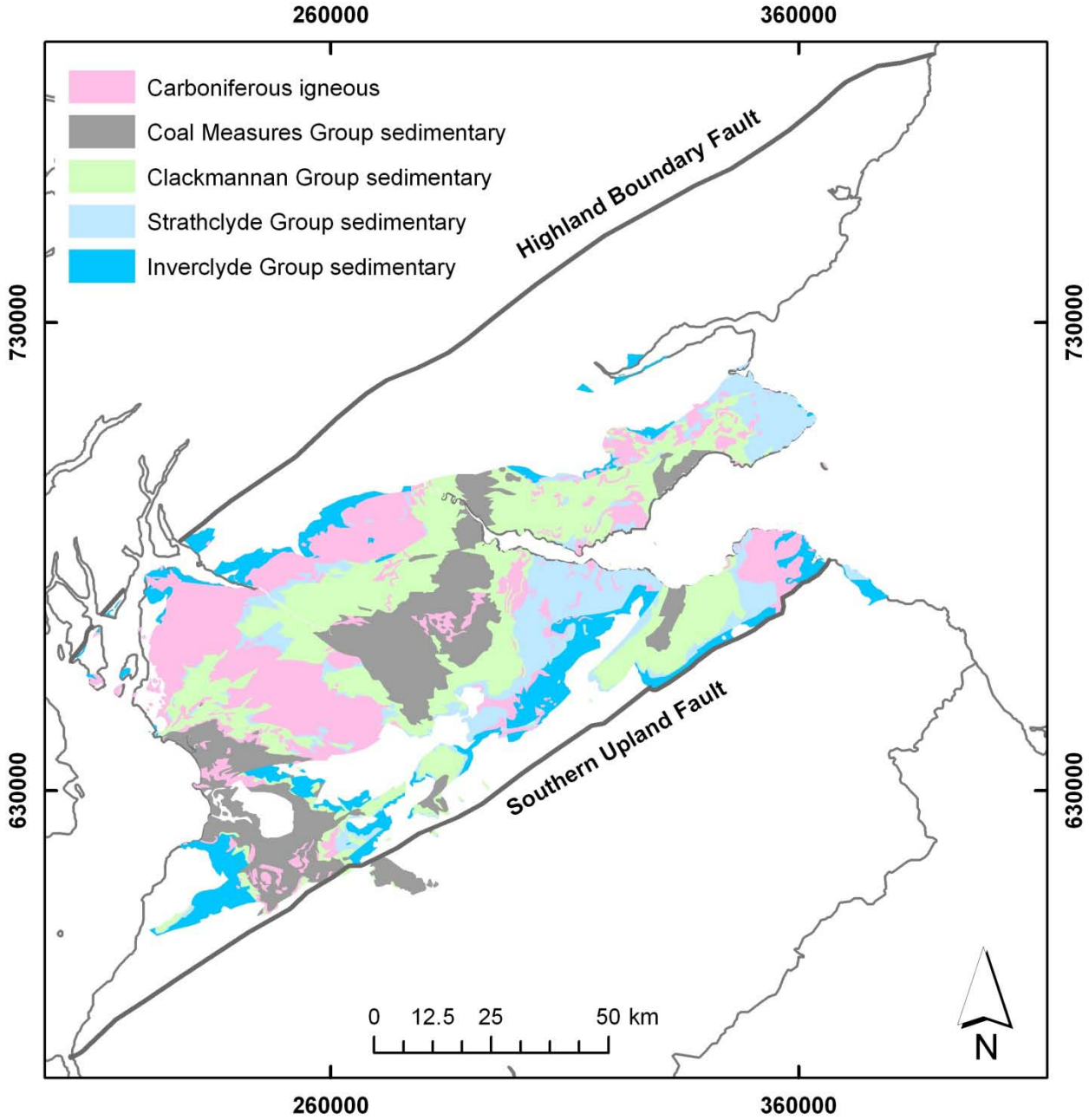


Figure 3 Bedrock geology (from 1:625 000 scale DigMap linework) of the Carboniferous rocks of the Midland Valley

2.3 SUPERFICIAL DEPOSITS GEOLOGY

Much of the Carboniferous aquifer outcrop is overlain by superficial deposits, except for the areas of highest ground. The main deposit type is glacial till, which tends to be clay-rich and compacted. On higher ground some extensive areas of peat have developed. The largest of the active river valleys, which typically acted as conduits for post-glacial meltwater, are infilled with glaciofluvial sand and gravel, overlain by alluvium. Raised marine deposits are important in many modern coastal areas, and extend inland along the Forth, Clyde and Tay estuaries, where they can be tens of metres thick. They include both granular and clay-rich deposits. Blown sand deposits are locally important, particularly in northeast Fife, as well as on the coast of East Lothian and Ayrshire.

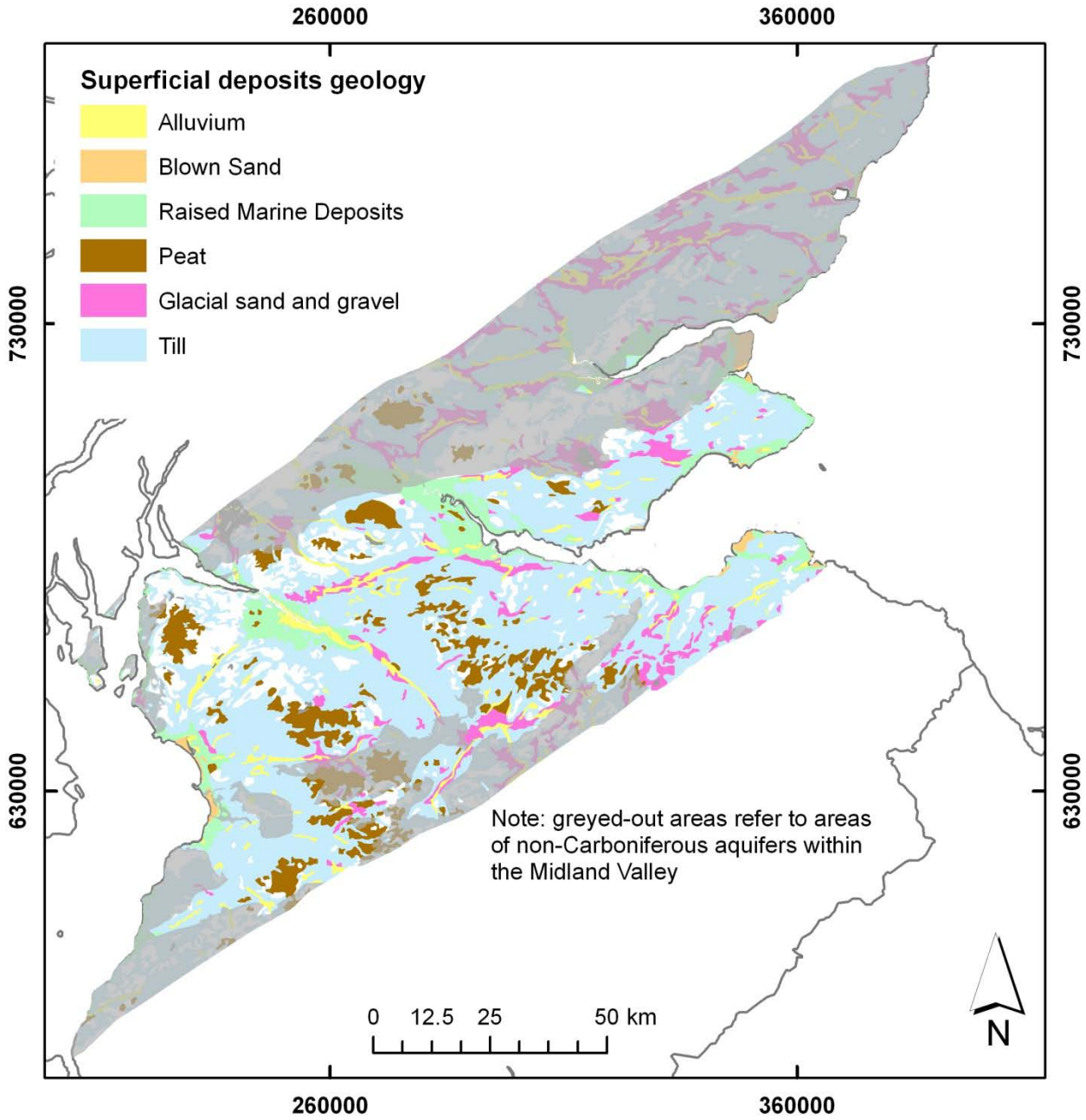


Figure 4 Superficial deposits (from 1:625 000 scale DigMap linework) in the Midland Valley. The areas outwith the current study are greyed out.

2.4 HYDROGEOLOGY

2.4.1 Bedrock hydrogeology

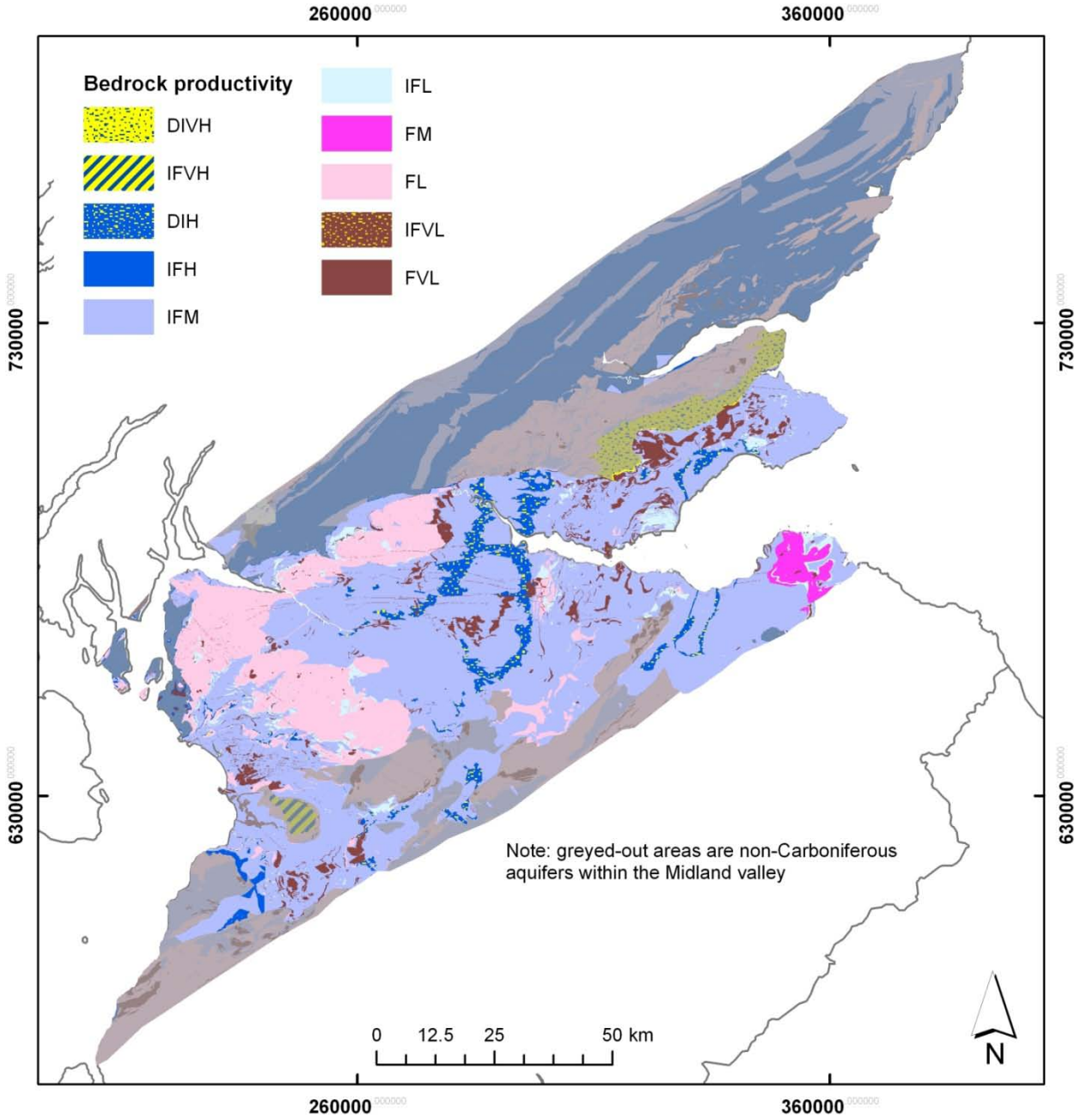
The hydrogeology of the Carboniferous sedimentary aquifers in the Midland Valley is complex. The cyclical sedimentary sequences of alternating fine- and coarse-grained rocks form multi-layered aquifers in which sandstone units effectively act as separate aquifers, interspersed with lower-permeability siltstones and mudstones. Some of these aquifers are effectively confined by overlying low permeability rocks. The hydrogeological complexity is increased by the predominance of fracture flow, and by the compartmentalising of groundwater flow within fault-bounded blocks.

Despite the widespread historical use of groundwater from Carboniferous aquifers in the Midland Valley, there are limited aquifer properties data. The Scottish Aquifer Properties Database holds only five values for transmissivity and three for storativity of the Carboniferous aquifer, all from Fife. The database also contains 46 specific capacity values, 37 matrix (from

core samples) hydraulic conductivity values and 34 matrix porosity values. The five recorded transmissivity values range from 70 to 760 m^2/day, with a median of 150 m^2/day and a mean of 319 m^2/day. These are from the highly permeable Kinesswood Formation, and are not representative of other Carboniferous formations. The three storativity values are 0.0003, 0.003 and 0.005. The specific capacity values range from 0.33 m^3/day/m to 1320 m^3/day/m, with a median of 52 m^3/day/m and a mean of 134 m^3/day/m. Measured matrix porosity ranges from 0.3 % to 23.7 %, with a mean of 14.4 %. Measured horizontal hydraulic conductivity ranges from 6.4 x 10^{-7} m/d to 1.41 m/d, with a median of 0.05 m/d and a mean of 0.21 m/d.

Recorded yields from boreholes in Carboniferous aquifers, also from the Scottish Aquifer Properties Database, range from zero (borehole reported as dry) to 22,248 m^3/day, with a median of 328 m^3/day and a mean of 1326 m^3/day. Recorded borehole yields are dependent on a number of factors as well as aquifer productivity – such as pump size and water demand – and these values should therefore only act as an indication of potential aquifer yields. The highest yields are likely to derive from boreholes intercepting mine workings, which have artificially increased the aquifer permeability and therefore productivity.

Overall, however, the Carboniferous sedimentary aquifers generally form moderately productive aquifers (Robins 1990; MacDonald et al. 2005a) (Figure 5). Groundwater flow is dominantly through fractures, even within the sandstone units, which are typically fine-grained, well-cemented and extremely hard and dense, and in consequence show low primary porosity and intergranular permeability. One notable exception is the Passage Formation, which is classed as a high productivity aquifer: it is dominated by more loosely-cemented sandstone, and has higher permeability and an increased proportion of intergranular flow (Robins 1990; MacDonald et al. 2005a). Other than the Passage Formation, the available information is usually not sufficient to rigorously distinguish differences in productivity between the different Carboniferous formations. However Ball (1999) assessed the formations of west-central Scotland based on the average yield of known abstraction boreholes in use. The average yield for boreholes in the Passage Formation was 4 to 10 l/s; for the Limestone, Limestone Coal and Coal Measures formations, 1 to 2 l/s; and for the Strathclyde and Inverclyde groups, 1 l/s. Many of the Carboniferous aquifers have been extensively impacted by mining. This is discussed further in Section 2.4.4.



DIVH	dominantly intergranular flow, very high productivity	FM	fracture flow, moderate productivity
IFVH	intergranular/fracture flow, very high productivity	FL	fracture flow, low productivity
DIH	dominantly intergranular flow, high productivity	IFVL	intergranular/fracture flow, very low productivity
IFH	intergranular/fracture flow, high productivity	FVL	fracture flow, very low productivity
IFM	intergranular/fracture flow, moderate productivity		
IFL	intergranular/fracture flow, low productivity		

Figure 5 Productivity of the Carboniferous aquifers in the Midland Valley (after MacDonald et al. 2004). The areas outwith the current study are partially greyed out.

2.4.2 Superficial deposits hydrogeology and groundwater vulnerability

Coarse-grained superficial deposits are relatively rare in the Midland Valley and confined to only a few areas. In central Fife spreads of glaciofluvial gravels occur, which are generally not restricted to river valleys. Elsewhere, alluvial and glaciofluvial deposits tend to form linear outcrops, either within existing river valleys or within former channels that no longer form part of the current drainage system. The most prominent of the latter is a deep buried channel that runs roughly west-east from just north of Glasgow, starting in the Kelvin valley, towards the

Forth estuary. Borehole data shows that this exceeds 100 m deep in parts**,** with a significant component of sand and gravel. The main deposits in river valleys are along the River Clyde, some of its tributaries to the south of Lanark, including the Douglas Water, and the rivers South and North Esk and some other nearby channels to the south of Edinburgh.

The detailed lithology of most of these deposits is unknown, but many are likely to be dominated by coarse sand and gravel, with varying amounts of finer-grained silt and clay grade material. Particularly where dominated by coarse-grained material, these deposits are likely to form permeable local aquifers in which groundwater infiltration and throughflow are often rapid. Shallow water tables in the low-lying deposits adjacent to the rivers mean there can be considerable volumes of groundwater storage in the deposits, particularly where the deposits are thick. The Kelvin buried channel in particular is likely to contain a very large volume of groundwater, although there has been no investigation of the groundwater resource there.

Flow paths in these superficial aquifers may vary from short to long, and from predictable and relatively straightforward to tortuous, depending on the three-dimensional geometry of the deposits and the degree of heterogeneity in their lithology and extent. The aquifer recharge potential is likely to be high, because their high permeability and location in valleys and lower ground means they capture a significant proportion of rainfall runoff towards the main surface watercourses. Alluvial aquifers are an important storage sink for groundwater before it discharges as baseflow to rivers, sometimes after several years. The terraces often formed by glaciofluvial sheet deposits on higher ground on valley sides, and the mounded ice-contact deposits, mostly lie above the water table. Although these do not therefore contain significant groundwater storage, their high permeability allows rapid groundwater infiltration and throughflow and they can play an important role in the local groundwater system by providing baseflow to rivers and wetlands.

The widespread till deposits are generally fine-grained and contain significant amounts of clay, particularly where they overlie mudstone units. They are also relatively dense, having often been compacted by ice action, and therefore have correspondingly low permeability and storage. Relatively small groundwater seepages are likely to occur throughout sandier and gravellier horizons in the till, sometimes feeding small springs where these horizons crop out at the ground surface.

Raised marine deposits are significant along the Forth and Clyde estuaries, and along parts of the coast, such as north of Ayr, around Edinburgh, and in southeast Fife. Along the two major estuaries these are dominantly fine-grained, clay-rich deposits, and are often more than 20 m thick. Along the coast in other areas, the deposits are generally thinner and dominated by sands.

Groundwater in the high-permeability, unconfined superficial deposits aquifers is typically highly vulnerable to pollution from surface and near-surface activities. Groundwater in bedrock underlying superficial aquifers is also likely to be vulnerable to pollutant transport through the overlying aquifers. Away from these superficial aquifers, the compact, clay-rich glacial till will offer protection to the underlying aquifers. Thick sequences of dominantly low-permeability raised marine deposits will provide significant protection to underlying groundwater, which is consequently likely to have low vulnerability to contamination (Ó Dochartaigh et al. 2005).

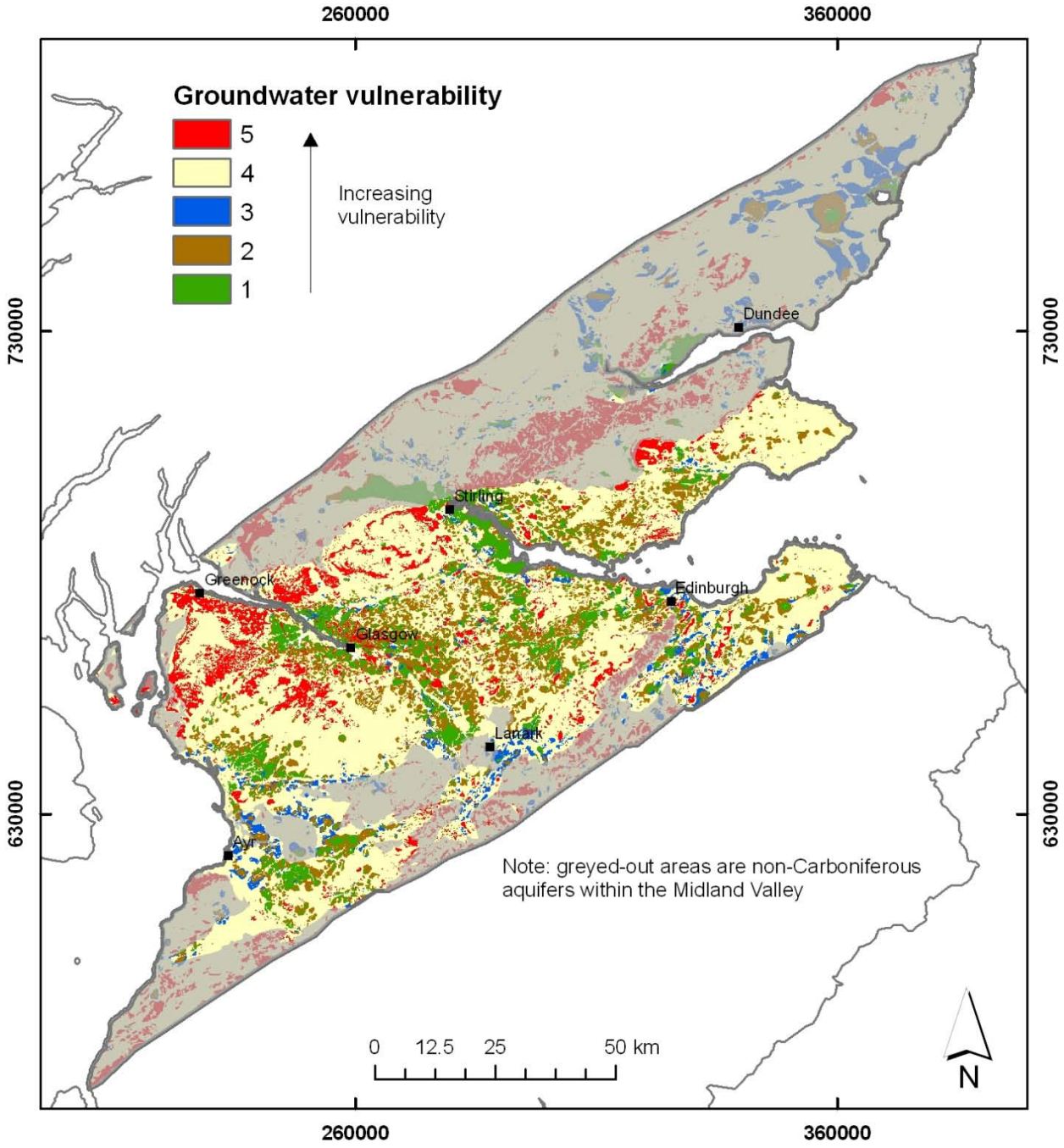


Figure 6 Groundwater vulnerability in the Midland Valley (from Ó Dochartaigh et al. 2005).

2.4.3 Groundwater abstraction and use

Historically, groundwater from Carboniferous aquifers in the Midland Valley was intensively used to support industry, particularly brewing, but also activities such as paper making, chemical processing, iron and steel making, and shipbuilding. Large-scale groundwater abstraction probably began in the 19th century, but is thought to have reached a peak in the 1950s (Robins 1990). Today, groundwater from the Carboniferous is used mainly for agriculture. In Fife and East Lothian this is largely for irrigation, and in the south and west of the Midland Valley largely for sheep and cattle. Groundwater abstraction for dairy farming is particularly widespread in Ayrshire.

Groundwater abstraction for mine dewatering was also extensive. Little information exists on the volumes of groundwater pumped from mines during dewatering operations, but a recent estimate put the total volume of groundwater being pumped from mines in the lower Clyde catchment

alone (largely the greater Glasgow and Lanarkshire areas) around 1950 at 215 Ml/d (Ó Dochartaigh et al. 2007). Robins (1990) states that the peak of mine water abstraction was likely to have been in the early 1960s, and Harrison (1982) suggests the total abstraction then from coal mines in the Carboniferous of the Midland Valley could have been 640 Ml/d. Robins (1990) estimated the volume of groundwater pumped from both deep and opencast coal mines in Scotland (all of which were in Carboniferous aquifers in the Midland Valley) in 1980, long after the peak of mining activity, at 258 Ml/d.

2.4.4 Mining

There is a long and extensive history of mining from Carboniferous sedimentary rocks of the Midland Valley. Although all deep mining in the region has now ceased, the impacts of mining continue to be the biggest influence on the hydrogeology of the Carboniferous aquifers. For many decades, mining, particularly for coal, was the major source of employment in much of the region, and was the backbone of Scotland's industrial and economic development from the late 18th to the mid 20th centuries. Scottish coal production, almost entirely within the Midland Valley, peaked in 1913 at approximately 44 million tonnes annually (Younger 2001). Polkemmet colliery was the last deep mine to close in 1985 (Chen et al. 1999). Most of the Midland Valley is underlain by extensive former mining operations (Figure 7).

As well as coal, mining was carried out for oil shale, fireclay, ironstone and limestone. Sandstone quarrying for high-quality building stone was also widespread. Both underground (shallow and deep) and open-cast mining was important, and open-cast mining is still being carried out, at various scales, across the region.

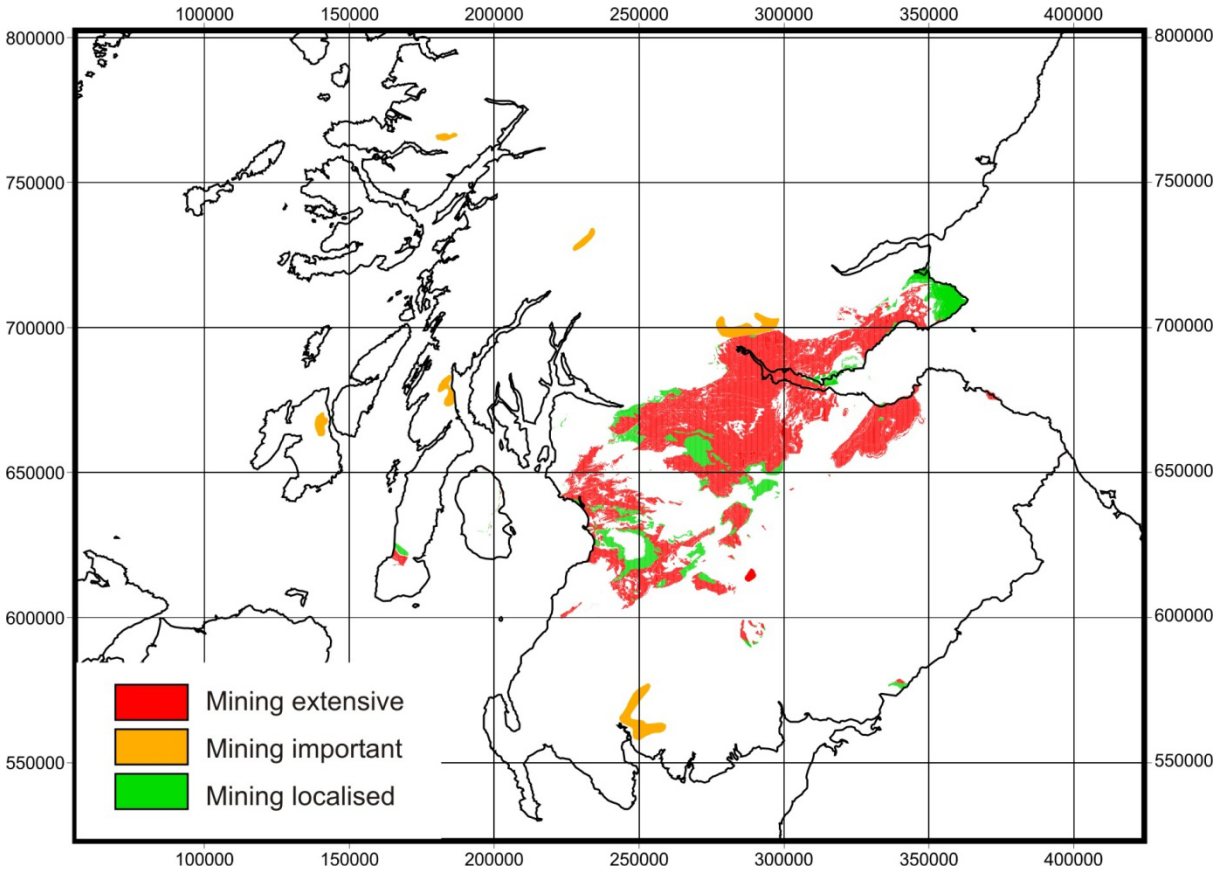


Figure 7 Areas of Scotland where shallow mining (< 200 m) has occurred), estimated from the outcrop of various geological formations and from data in the BGS mineral occurrences database (after MacDonald et al. 2003)

An unknown but large volume of the Carboniferous aquifers has experienced varying degrees of alteration as a result of mining. There are several ways in which aquifers can be affected by mining:

Mine voids (shafts and tunnels) can artificially and hugely increase the transmissivity of aquifers, sometimes across large areas and depths, and formerly separate groundwater flow systems can be linked, both laterally and vertically. Storativity can also be locally increased. Deformation of the surrounding rock mass due to void collapse can cause further changes in transmissivity and, to a lesser degree, storativity (Younger and Robins 2002).

During coal mining in the Midland Valley and for many years after mines are closed, mine dewatering caused large volumes of groundwater to be pumped to the surface and discharged (see estimates in Section 2.4.3, above). The drawdown of water levels and exposure of rock strata to air during mine dewatering causes changes in the oxidation state of rock minerals, increasing their solubility. Of particular concern is pyrite, which when first exposed and later flooded causes large concentrations of Fe and SO_4 to be mobilised, producing acidity. Water chemistry can be further altered by the presence of carbonate minerals, which react to buffer pH.

The quality of mine water is typically worst during the early years (up to three or four decades) of mine water discharge and groundwater rebound at any site, and generally improves with time (Younger 2001). There are currently eleven mine water treatment schemes in the Midland Valley of Scotland, where discharging water is monitored and controlled where necessary (Coal Authority 2010). Net-alkaline ferruginous mine waters (where acidity has been buffered by the dissolution of carbonate minerals) are the most common source of pollution, and these are predominantly associated with flooded deep mine workings, particularly coal mines, in the Carboniferous aquifers of the Midland Valley (Younger 2001). Acidic polluted mine waters are far rarer in Scotland than alkaline waters, and are most commonly associated with unreclaimed spoil heaps (known as bings) (Younger 2001).

Monitoring of water levels has occurred in many mines since dewatering was stopped, particularly since the early 1990s. Data from the East Fife Coalfield show that water levels in the deepest mines, including Frances colliery, were recovering by some 20 m per year during the late 1990s, following the cessation of mine water pumping in 1995 (Whitworth 2002). At Polkemmet Colliery in West Lothian, data from the ten years after dewatering stopped in 1984 suggested that groundwater rebound was occurring at up to 10 m per year (Chen et al. 1999). A database of some 150 abandoned mines where minewater is still pumped or, more commonly, discharges by gravity flow to the surface, is maintained by the Coal Authority. Some monitoring is carried out on these sites, related to the size of the flow and the known groundwater chemistry (Coal Authority 2010). Most of the flows are small, less than 5 l/s.

2.5 AQUIFER GEOCHEMISTRY FROM BGS GEOCHEMICAL SURVEYS

2.5.1 Stream sediment information

An assessment of the mineralogy of the aquifers in the study area has been made based on stream sediment geochemistry collected and analysed as part of the BGS national Geochemical Baseline Survey of the Environment (G-BASE) project (British Geological Survey 1993). Below are outlined patterns in selected element distribution inferred from stream sediment geochemistry.

Calcium (as CaO) in stream sediments in the Midland Valley is relatively enriched (2–4%) on many of the volcanic rocks, such as the basic lavas of the Clyde Plateau. It is also relatively high over the Inverclyde and Strathclyde groups in the east of the area, often reflecting a high proportion of cornstones and calciferous cement in the sedimentary rocks. Over the younger Clackmannan and Coal Measures group rocks, CaO in stream sediments is generally lower (*ca* 2%).

The highest magnesium (as MgO) values (*c.* 6%) are also associated with basic Clyde Plateau and other lavas. By contrast, low MgO values (1–2%) occur over most of the Carboniferous sedimentary rocks. Particularly low concentrations (<0.75%) overlie Clackmannan Group rocks east of Edinburgh.

Generally low arsenic (As) concentrations occur across the Midland Valley, typically <4–5 mg/kg. The most notable anomaly is more than 140 mg/kg at a volcanic-sedimentary contact near Linlithgow west of Edinburgh, thought to be associated with mineralisation caused by late-Carboniferous hydrothermal veins cutting through the sedimentary rock.

Iron concentrations (as Fe_2O_3) in stream sediments are highest (>15 wt%) over the Clyde Plateau lavas. They are typically low (<10 wt%) over the predominantly non-clastic sedimentary Carboniferous rocks, but high values (10–25 wt%) occur intermittently over the Coal Measures north and east of Glasgow.

Stream sediments overlying Carboniferous sedimentary rocks have moderate lead (Pb)concentrations (40–90 mg/kg). Relatively high concentrations (>60 mg/kg) occur locally over the coalfields in Fife, and extremely high values (>260 mg/kg) occur around Kirkcaldy. These are linked to contamination associated with mining. Values above 260 mg/kg also occur at Alva near Stirling, thought to be associated with small Pb-Zn veins. High Pb values (>150 mg/kg) also occur around the urban margins of Glasgow and Edinburgh.

Uranium (U) concentrations in stream sediments are low (<1.0 mg/kg) over the Clyde Plateau lavas. Concentrations over Lower Carboniferous sedimentary rocks reflect the proportion of quartzo-feldspathic, organic and calcareous material. Low or moderate values (1.5–4 mg/kg) overlie the Clackmannan, Strathclyde and Inverclyde groups in the eastern half of the Midland Valley. Sediments over the Coal Measures Group in the west of the Midland Valley are more enriched in U, typically around 4 mg/kg.

2.5.2 Stream water information

Limited stream water chemistry information (pH, conductivity, alkalinity and fluoride concentration) was also collected by the BGS G-BASE project during sampling of stream sediments (British Geological Survey 1993). Patterns from stream water chemistry are outlined below.

High pH stream waters (7.5–8.0) dominate over much of the Lower Carboniferous calcareous sandstones and limestones east of Edinburgh and in eastern Fife, while more acid conditions (<6.0) prevail over the Coal Measures Group east of Glasgow. A small group of acidic waters (pH <6) between Dunfermline and Alloa are associated with mining.

Land use can also have an important effect on the pH of surface waters: in agricultural areas, such as east of Edinburgh, the use of lime and other basic fertilisers is likely to have contributed to a higher pH, while the planting of coniferous forests on higher ground may significantly reduce the pH by reducing the acid-neutralising buffering capacity of soils.

Stream waters with highest conductivities (>500 µS/cm) are generally seen over Carboniferous Clackmannan and Strathclyde group rocks east of Edinburgh and in areas of extensive Coal Measures in Ayrshire. Higher conductivities (>400 µS/cm) occur along the coastal areas of Fife, partly attributable to seawater spray but also associated with Lower Carboniferous calcareous sandstones and limestones and industrial pollution along the Firth of Forth. High values (>500 µS/cm) linked to pollution are especially clear northeast of Kirkcaldy and west of Dunfermline, linked to the acid waters mentioned above.

Relatively high alkalinity values in stream water (200–400 mg/L) occur over most of the Carboniferous sedimentary rocks, the highest values associated with limestones and calcareous sandstones.

Fluoride concentrations in stream waters are relatively high (0.1–0.2 mg/L) in the Midland Valley compared to the surrounding areas, linked to the presence of Upper Carboniferous sedimentary rocks, including limestone and coal facies, and volcanic rocks. Around Glasgow, this enrichment may be compounded by industrial activity.

2.6 RAINFALL CHEMISTRY

The UK Air Quality Data Archive (http://www.airquality.co.uk/archive/index.php) has no rainfall chemistry monitoring stations in the Midland Valley. The closest monitoring stations are at Whiteadder to the southeast of the Midland Valley in the Lammermuir Hills, and at Loch Chon to the northwest near Loch Lomond. Annual average rainfall at Loch Chon, in the wetter west of the country, is three times higher than at Whiteadder, despite the fact that the Loch Chon site is at a lower elevation.

Solutes derived from rainfall typically increase during evapotranspiration, such that the solute concentration in infiltrating recharge in the UK is typically expected to be roughly three times higher than in rainfall (e.g. Appelo and Postma, 1993). However, nutrient concentrations (e.g. nitrogen (N) and potassium (K)) may decrease due to biomass uptake, so that infiltrating (recharge) waters may contain lower concentrations of these solutes than the evaporated rainfall. Ammonium would be expected, at least partially, to oxidise to nitrate on infiltration. The composition of infiltrating recharge to the Carboniferous aquifers is therefore difficult to establish. However, an estimate taking account of likely evapotranspiration, based on a three times concentration of the median rainfall chemistry from available records at Whiteadder and Loch Chon is presented in Table 1.

Table 1 Rainfall chemistry at monitoring stations close to the Midland Valley, from the UK National Air Quality Information Archive (http://www.airquality.co.uk/archive/index.php)

	Units	**Whiteadder**	**Loch Chon**	Expected chemistry of infiltrating recharge after evapotranspiration[4]
NGR		NT 365 664	NN 420 706	
Elevation	m OD	250	100	
Annual rainfall	mm	591[1]	1789[2]	
		Median concentration in rainfall 1987–2007[3]	Median concentration in rainfall 2000–2007	
pH		4.66	4.96	n/a
SEC	µS/cm	29	21	75
Ca	mg/L	0.28	0.12	0.6
Cl	mg/L	2.53	2.18	7.07
K	mg/L	0.11	0.09	0.3
Mg	mg/L	0.22	0.15	0.56
NH_4-N	mg/L	0.30	0.20	n/a
NO_3-N	mg/L	0.34	0.2	1.56
Na	mg/L	1.52	1.29	4.22
SO_4-S	mg/L	0.70	0.39	1.64

[1]Mean annual rainfall 1987–2007 (no data for 2001).
[2]Mean annual rainfall 2000–2007
[3]No data for 2001
[4]Calculated for illustrative purposes as three times the median rainfall concentration averaged across the two monitoring stations; assumes all NH_4 oxidises to NO_3.

3 Methodology

3.1 INTRODUCTION

A total of 62 groundwater chemistry analyses were used to interpret the groundwater chemistry of the Carboniferous aquifers of the Midland Valley. Of these, 36 were from new groundwater samples collected for the Baseline Scotland project in September and December 2008. One sample was collected during an earlier Baseline Scotland sampling programme in the Borders. These were augmented with a further 25 samples collected during separate projects: ten in April and May 2005 as part of a project to review the effectiveness of Scotland's national groundwater nitrate monitoring network (MacDonald et al. 2005b); 11 during November 2001 as part of a project to identify suitable points for groundwater sampling in areas proposed as nitrate vulnerable zones (NVZ) (Ball and MacDonald 2001); two during November 2004 as part of a survey of spring sources (Ball et al. 2006); and two in January 2006 as part of a small groundwater resource investigation (Ó Dochartaigh 2006). These earlier samples fill in many of the spatial gaps in sample collection across the study area.

3.2 SITES SAMPLED

The sites for all samples used in the study were chosen to be representative of groundwater in the local area. Sources that were poorly constructed (e.g. open and/or uncased boreholes in leaking chambers) or which were close to obvious and significant sources of contamination (e.g. unsecured slurry stores) were avoided. Each of the sample sites was assessed at the time of sampling, in particular the source construction and the surrounding land use, to identify any potential sources of contamination that could affect the chemistry of sampled groundwater and the risk of contamination.

The location of the sampling points is shown in Figure 8. Details of the distribution of samples across source type, aquifer and land use are given in Table 2. Most of the samples were collected from boreholes. In most cases, the sampled boreholes had been pumped regularly in the few weeks leading up to sampling, and were pumping at the time of sampling. Hence, groundwater samples were believed to be as representative of groundwater in the aquifer as possible. Where boreholes were not pumping on arrival, they were pumped for at least 10 minutes (and usually 30 minutes) to allow purging before sample collection. Pumped groundwater samples represent the compositions of water entering the borehole over its open-hole section. As such, the sample may represent a mixture of waters with different chemistry, especially where the borehole screen extends over more than one fracture inflow.

Six of these samples were collected from boreholes, shafts or adits directly tapping coal mine workings (Figure 8). Four others are known to be from boreholes that intercept abandoned mine workings; a fifth was collected from an adit of a former non-coal mine. Away from these sample sites, the effect of mining on local groundwater flow systems is unknown. Where they exist, abandoned mine workings may have significantly increased aquifer permeability and may have enhanced groundwater mixing, but it is not possible to positively identify where this may have occurred.

Six of the samples were collected from springs (although one of these – Sample 18 (Figure 8) – was difficult to identify in the field, and may be an artesian borehole rather than a spring). One sample was collected from a shallow well. The large diameter of shallow wells means it can be difficult to ensure that the well is sufficiently purged before sampling so that a representative sample can be obtained. However, the sampled well is in daily use for drinking water supplies, and is therefore regularly pumped, and likely to give a representative groundwater sample. Springs are constantly flowing and therefore are naturally purged. Both springs and wells typically tap shallow groundwater and have relatively small catchments, and so are less likely than boreholes to represent a mixture of groundwaters from different depths.

3.3 SAMPLING PROCEDURE

For the samples collected specifically for this study, sampling methodology is described below. For previous surveys, methodologies are given in references cited in Section 3.1. At each sample site chosen for the study, field measurements were made of pH, dissolved oxygen (DO), redox potential (Eh), water temperature, specific electrical conductance (SEC) and alkalinity. Where possible, pH, DO and Eh were measured in an in-line flow cell to minimise atmospheric contamination and parameters were monitored (typically for 10 to 15 minutes) until stable readings were obtained. Where not possible, measurements of water direct from the pump outlet were made in a bucket within one to two minutes of water abstraction.

Water samples were collected from each site for subsequent laboratory analysis. Analyses were carried out at the BGS/CEH laboratories in Keyworth and Wallingford. Samples for major and trace element analysis were filtered through 0.45 μm filters and collected in factory-new polyethylene bottles rinsed with sample water before collection. Three filtered aliquots were collected at each site. Two were acidified to 1% v/v with Aristar HNO_3, one for analysis of major cations, total sulphur and Si by ICP-OES (inductively coupled plasma-optical emission spectroscopy), and the other for a large range of trace elements by ICP-MS (inductively coupled plasma-mass spectrometry). A third aliquot was left unacidified for analysis of anions by ion chromatography (NO_3-N, Cl, Br, F) and automated colorimetry (NH_4-N, I). Samples were also collected in chromic-acid-washed glass bottles for dissolved organic carbon (DOC) analysis, after filtration using silver-impregnated 0.45 μm filters. DOC was measured by carbon analyser. At 15 of the sample sites, additional samples were collected in glass bottles for stable-isotopic analyses (δ^2H, $\delta^{18}O$ and $\delta^{13}C$-DIC). Analysis was carried out by mass spectrometry. At nine of the sites, a sample for CFC and SF_6 analysis was also collected in a glass bottle, submerged under flowing groundwater to prevent atmospheric contamination. Samples for the dissolved gases CO_2 and CH_4 were collected at 26 sites, in steel sampling containers that allow sample collection without exposure to the atmosphere.

Analyses of total sulphur are hereafter expressed as SO_4 and alkalinity as HCO_3. Analyses of δ^2H, $\delta^{18}O$ are expressed as per mil deviations relative to VSMOW (Vienna Standard Mean Ocean Water) and $\delta^{13}C$ in dissolved inorganic carbon (DIC) relative to VPDB (Vienna Pee Dee Belemnite).

The average absolute charge imbalance was +1.0%, and for all but two of the samples the maximum imbalance was +5.6%. The remaining two samples had charge imbalances of +7.1% and +21.1%. BGS laboratories run a series of QA checks, including analysis of certified standards, to ensure that analyses are within their prescribed limits. For the two samples with highest imbalances, further investigations were made to establish the causes. For the sample with the highest imbalance (+21.1 %), the reason is believed to be an unreliable HCO_3 value: a field alkalinity titration was not possible for this sample due to excessive discoloration (i.e. high Fe content), and the sample is believed to have degraded (i.e. Fe(II) oxidised) before laboratory analysis of alkalinity was possible. The sample with imbalance of +7.1% is also believed to be due to an unreliable alkalinity, both from the field analysis, due to erroneous measurement caused by high Fe concentrations, and from laboratory analysis, due to Fe oxidation and loss of HCO_3 during sample storage.

Overall, the charge balances are good and the analytical data are considered reliable. To ensure confidence in the data, the two alkalinity values from the samples with the highest charge imbalances were omitted from the dataset for the subsequent interpretation, and are not referred to further in this report.

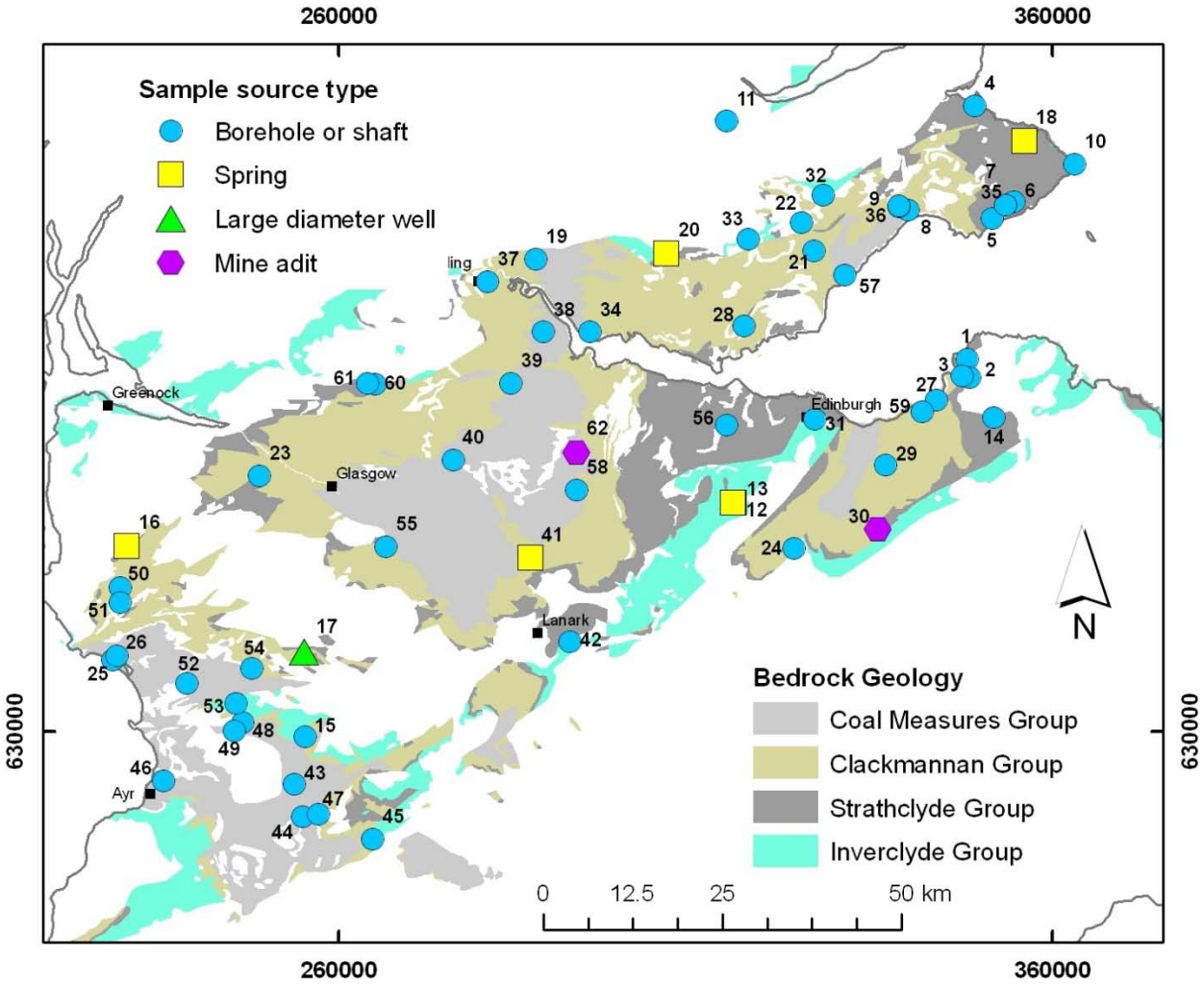


Figure 8 Location and reference numbers of groundwater samples in the Midland Valley (for details of reference numbers see Appendix 1)

Table 2 Summary of samples by geology, surrounding land use and source type

Land use	Arable			Improved grassland				Dairy, Pigs and/or Poultry			Mixed cultivated			Semi natural and woodland				Industrial / urban			Recreational			Total
Geology	B[1]	S[1]	W[1]	B	S	W	A[1]	B	S	W	B	S	W	B	S	W	A	B	S	W	B	S	W	
Coal Measures Group	2			1				3			1			1							2			10
Clackmannan Group	4	1		2		1	1	4			1			2				3	1		1			21
Strathclyde Group	5			1				2	1		1							2			4			16
Inverclyde Group											3			2	3			1						9
Coal mine	1																1	2		2				6
Total																								**62**

[1]B – Borehole; S – Spring; W – Well or Shaft; A – Adit

4 Hydrogeochemistry

4.1 DATA ANALYSIS AND PRESENTATION

4.1.1 Summary statistics

Groundwater quality data are available for a total of 62 sites distributed across the study area (Figure 8). The numerical ID for each sample in Figure 8 refers to a table providing summary details of each sample site (Appendix 1). Summary statistics were calculated for the whole dataset for each of the measured parameters (Table 3 in Section 5). These provide an indication of the range of values observed, and can be compared with similar tables from other areas. The median value provides the preferred estimate of the 'central tendency' for a particular dataset since it is less affected by extreme concentrations than the arithmetic mean. Summary statistics have been reported in terms of range and percentiles (minimum, 10^{th}, 25^{th}, 50^{th}, 75^{th}, 90^{th}, 95^{th} and maximum) to provide a non-parametric summary of the chemical distribution (Table 3). Data for many trace elements were close to or below their respective individual detection (or reporting) limits, which can complicate the calculation of summary statistics. The total number of observations and the number of censored (below detection limit) observations are also reported (Table 3), to indicate the degree of censoring. Two methods were used to generate summary statistics for datases with censored data. The non parametric Kaplan-Meier approach was used for most datasets; but where censoring was above 50% we used the "regression on order" approach (ROS) following the recommendations of Lee and Helsel (2007). For a discussion on the use of these methods in the Scottish Baseline project, and a comparison of these and other statistical approaches for dealing with censored data see MacDonald et al. (2008) Summary statistics for each of the separate aquifer groups have also been calculated and are reported in Appendix 2.

4.1.2 Maps

'Bubble' maps were used to display the spatial distribution of the various water-quality parameters. These were generated in R using the `PBSmapping` and `maptools` packages with shapefiles generated by ArcGIS®. A simplified geological base map, derived from the BGS 1:625,000 scale bedrock geology map, is presented with the groundwater chemistry information. In most cases, four classes were used to map the chemical parameters, with the size and colour of the plotting symbol varying with the class. Class limits were broadly based on the 25, 50 and 90 percentiles for the determinand range. These were simplified if there were insufficient distinct values to generate reliable percentiles.

4.1.3 Box plots

Box plots provide a quick graphical summary of the distribution of data values in a dataset and are an effective way of comparing different distributions. They provide a rapid view of the central location of the distribution (the median), the spread of values (box length is the interquartile range (IQR), i.e 25^{th} to 75^{th} percentile) and the presence of outliers (open circles beyond the whiskers, which extend to 1.5 times the interquartile range) (Figure 9). Note that the presence of outliers depends to some extent on the number of values summarised, as even perfectly 'normal' distributions can show outliers if there are sufficient values within the distribution, as in Figure 9. Helsel (2005) discusses how the classical box plot can be adapted for displaying distributions containing censored data.

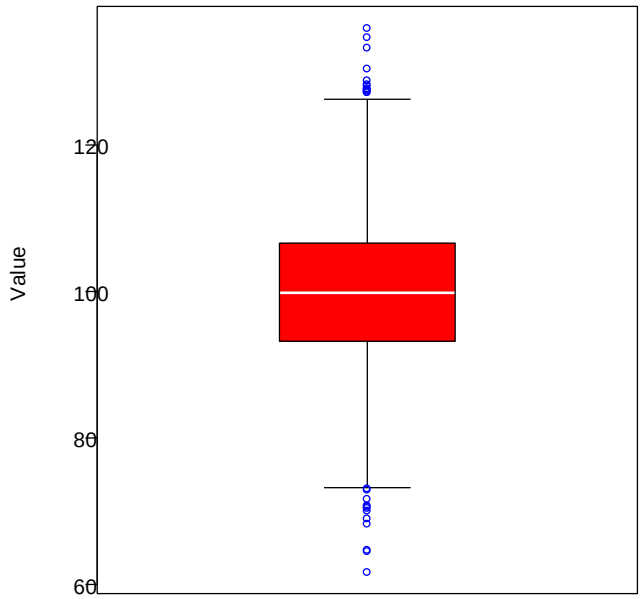


Figure 9 Example of an annotated box plot based on a simulated normal distribution of 2000 values with mean = 100 and standard deviation = 10. In this case, the whiskers are placed at no more than 1.5 × the interquartile range; outliers lie beyond this range.

4.1.4 Classifying the data

The data have been stratified mainly on the bedrock aquifer type from which the sample was taken, with a separate category for samples known to be derived directly from former coal mines. Four main chronostratigraphic aquifer categories have been used: in decreasing age order these are the Inverclyde Group, Strathclyde Group, Clackmannan Group and the Coal Measures Group. Some of the samples in these groups may also be impacted by coal mining: five of them (two from the Clackmannan Group and three from the Coal Measures Group) were collected from boreholes or shafts known or strongly suspected to intercept abandoned mine workings, although not drilled purposely for mine or mine dewatering purposes, and which are therefore likely to abstract at least in part from these workings. A fifth category, called 'Mine', includes six samples specifically collected from former coal mines.

In groundwater, the distribution of many elements, especially trace elements, tends to be closer to log-normal than normal. For this reason, concentration ranges for many of the elements were plotted on a log scale. This means that the occasional high outlier does not cause the scaling to obscure any low-concentration data on the box plots.

4.2 PHYSICO-CHEMICAL PARAMETERS AND ALKALINITY

The pH and redox conditions, as well as the concentrations of the major cations (Na, K, Ca and Mg) and anions (HCO_3, Cl, NO_3, SO_4) together define the basic hydrogeochemical nature of a groundwater. Compositions reflect the chemistry of the initial infiltrating rainfall (Section 2.6) and other surface inputs to the aquifer, together with outputs in the form of evaporation, and subsequent reaction of the groundwater with the aquifer mineral matrix.

In areas where surface inputs are relatively small and nearly constant, the spatial variation in groundwater chemistry will largely reflect variations in rock type. For elements where the contribution from the aquifer rocks is uniformly low, such as is the case with nitrate, variations in groundwater chemistry largely reflect variations in surface inputs – in the case of nitrate, from agriculture.

4.2.1 pH and alkalinity

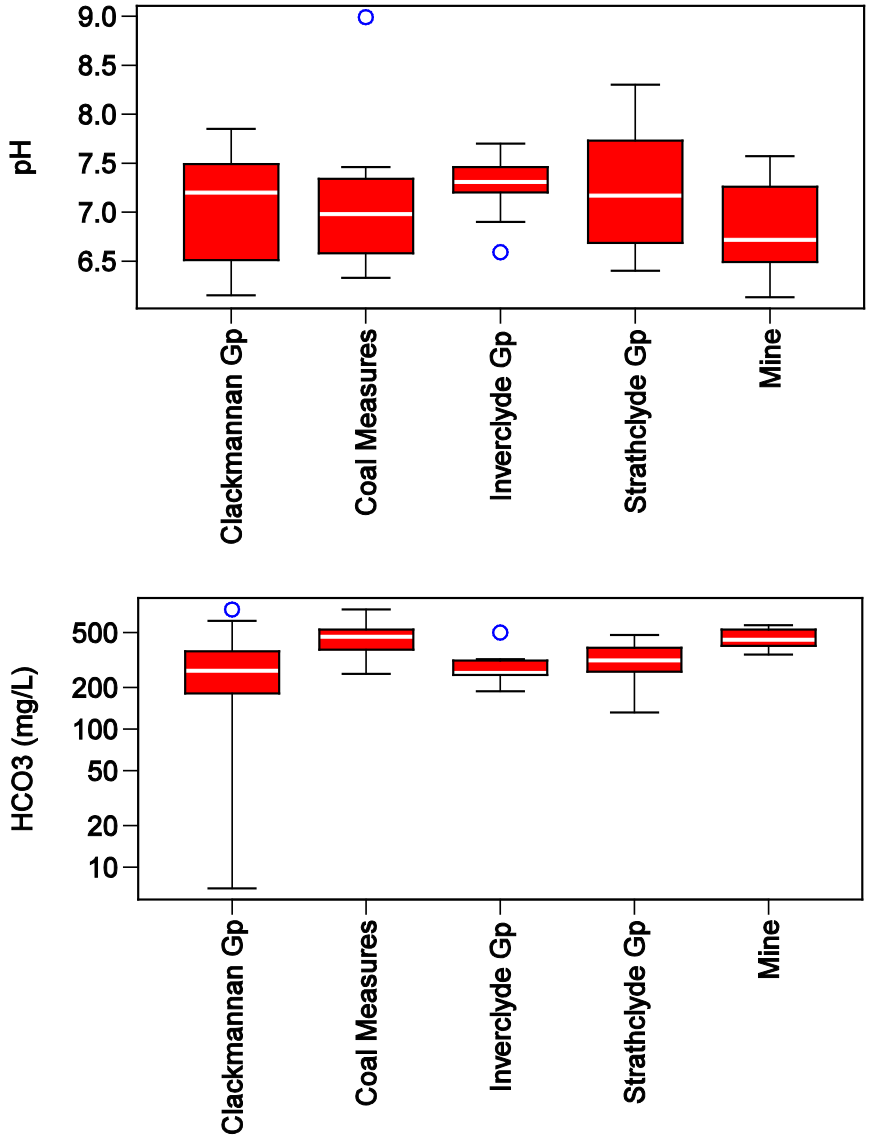
Most of the Carboniferous groundwater samples have a near-neutral pH, with a 10^{th}–90^{th} percentile range of 6.40 to 7.85 and a median of 7.2 (Table 3). There is little apparent difference between the aquifer types (Figure 10). The lowest pH value observed (6.13) was from a sample in the 'Mine' category (Sample 57). The median pH of 'Mine' waters is 6.61. The near neutrality of all samples, including specific mine discharges indicates the high acid buffering capacity of the aquifers, most likely by carbonate minerals.

A single high pH outlier, at 8.99, occurs in a sample from the Coal Measures on the Ayrshire coast (Sample 46), which has been subject to considerable water rock reaction and ion exchange of Na, and is known from field observation data to be affected by saline intrusion.

Given the near-neutral pH of most of the groundwaters, the main species contributing to the alkalinity is likely to be HCO_3. Bicarbonate concentrations are variable but often high, with a 10^{th}–90^{th} percentile range for the whole dataset of 132 to 510 mg/L. The highest median values are found in groundwaters from the Coal Measures Group and 'Mine' waters, although some high values also occur in groundwaters from the Clackmannan Group. This group has the widest range of HCO_3 concentrations (Figure 10), with one value as low as 7 mg/L (Sample 41). This latter sample was from a spring source and had a comparatively low SEC value (137 µS/cm); the water is likely to be of shallow circulation and short residence time, with consequently limited interaction with aquifer minerals.

As with pH, the presence of high-alkalinity waters in the Coal Measures and particularly the 'Mine' samples, suggests significant reaction with carbonate in the aquifer to neutralise the acidity produced by the dissolution of pyrite. Dissolution of silicate minerals (exacerbated by mine water influx) is also likely to be a source of increased alkalinity.

Maps of pH and alkalinity distribution (Figure 11) show a high degree of spatial variability with no distinct regional patterns.



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

Figure 10 Box plots showing the distribution of pH and alkalinity (as HCO_3, log scale) in groundwaters from Carboniferous aquifers across the Midland Valley

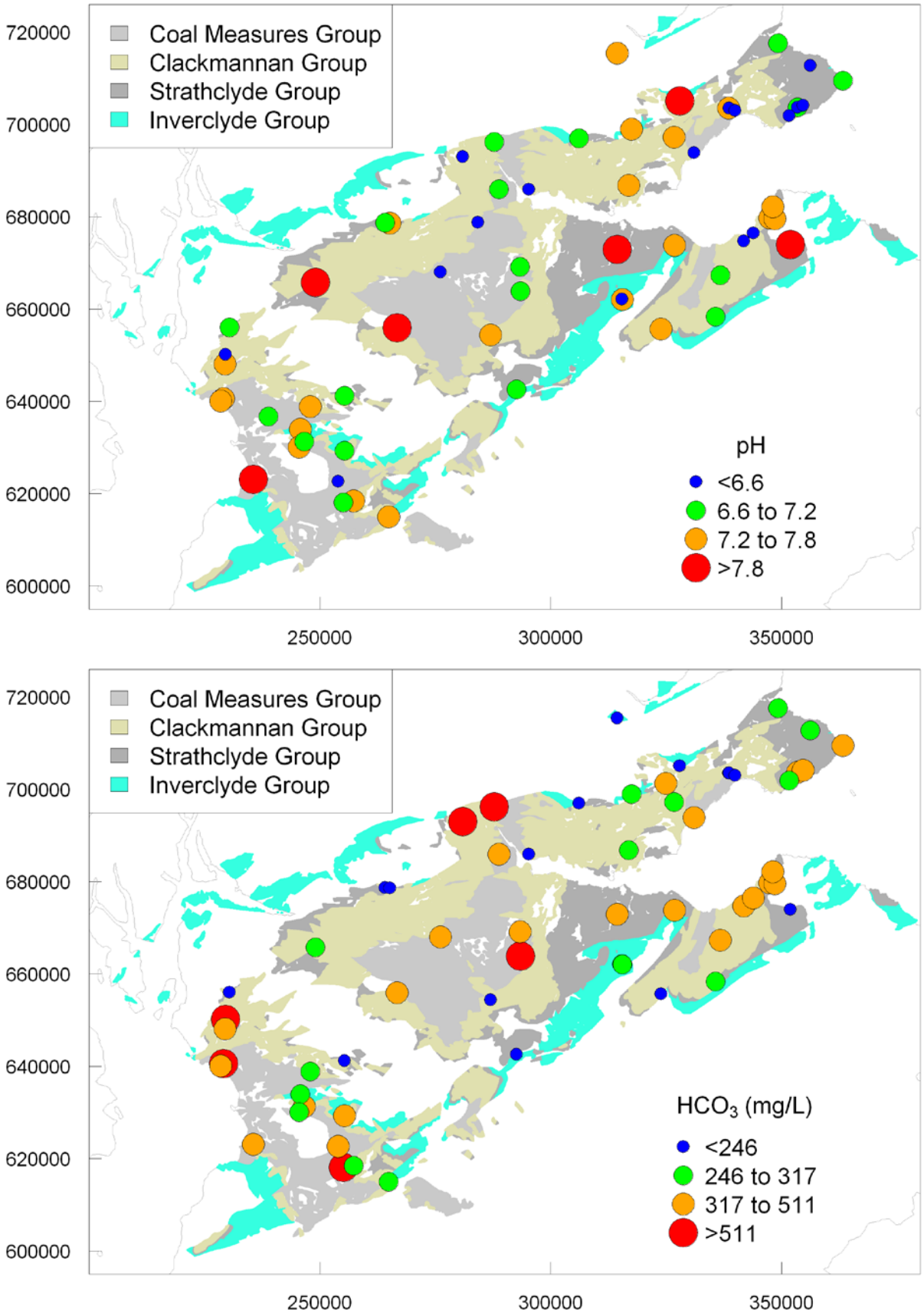


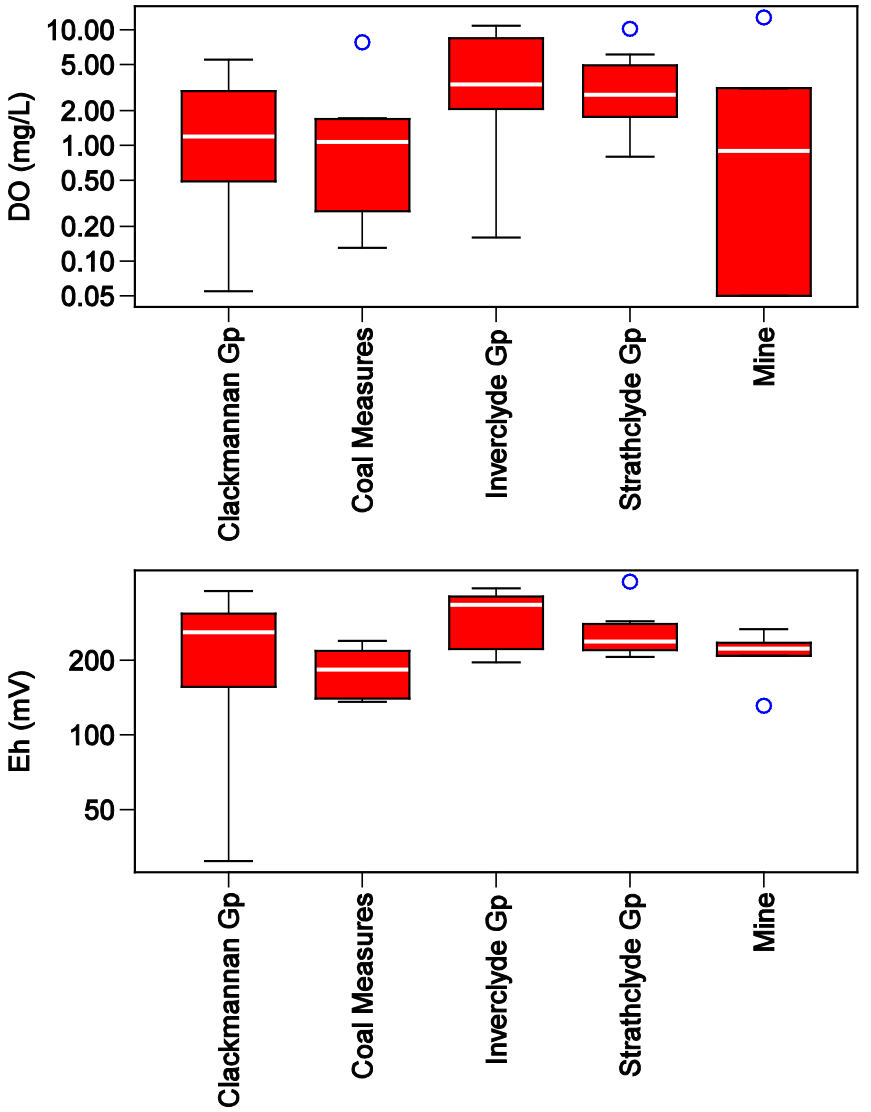
Figure 11 Maps showing the spatial distribution of pH and alkalinity (as HCO_3) in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

4.2.2 Dissolved oxygen and Eh

Many of the collected groundwaters are reducing (anoxic), with (where determined) 37% of samples having dissolved oxygen (DO) concentrations of ≤1 mg/L and 60% of samples having Eh values of less than 250 mV. The 'Mine' waters show particularly low DO concentrations (Figure 12), with 50% of the mine water samples (3 out of 6) having DO concentrations below the detection limit (<0.1 mg/L) and all but one have Eh values less than 250 mV. Many of the groundwaters from the Clackmannan Group and Coal Measures groups were also reducing (Figure 12). Three of the sources sampled were listed as artesian, all of which were from the Clackmannan Group and were reducing, with DO concentrations ≤1 mg/L. Field sampling showed evidence (by smell) that some of the groundwater sources from the Clackmannan and Coal Measures groups contained dissolved sulphide. This indicates the presence of strongly reducing conditions in some parts of these aquifers. Detectable dissolved methane was also measured in a number of the samples (Section 4.6.3).

Samples from the Strathclyde and Inverclyde groups show the highest DO concentrations (Figure 12). Redox potentials (Eh) do not show such clear distinctions between the different aquifer groups, although waters from the Inverclyde Group show the highest median Eh value (Figure 12).

The large range and commonly reducing nature of the waters indicates the variability in groundwater flow conditions, variable depth of groundwater sources (borehole, well or spring), abundance of reducing agents (sulphide minerals, organic matter) in the aquifers and the variable impact of poorly-permeable superficial drift deposits. No distinct spatial trends are apparent from maps of DO and Eh distribution (Figure 13). This is not unexpected given the spatial heterogeneity of the aquifers themselves.



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

Figure 12 Box plots showing the distribution of dissolved oxygen (DO) and redox potential (Eh) in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

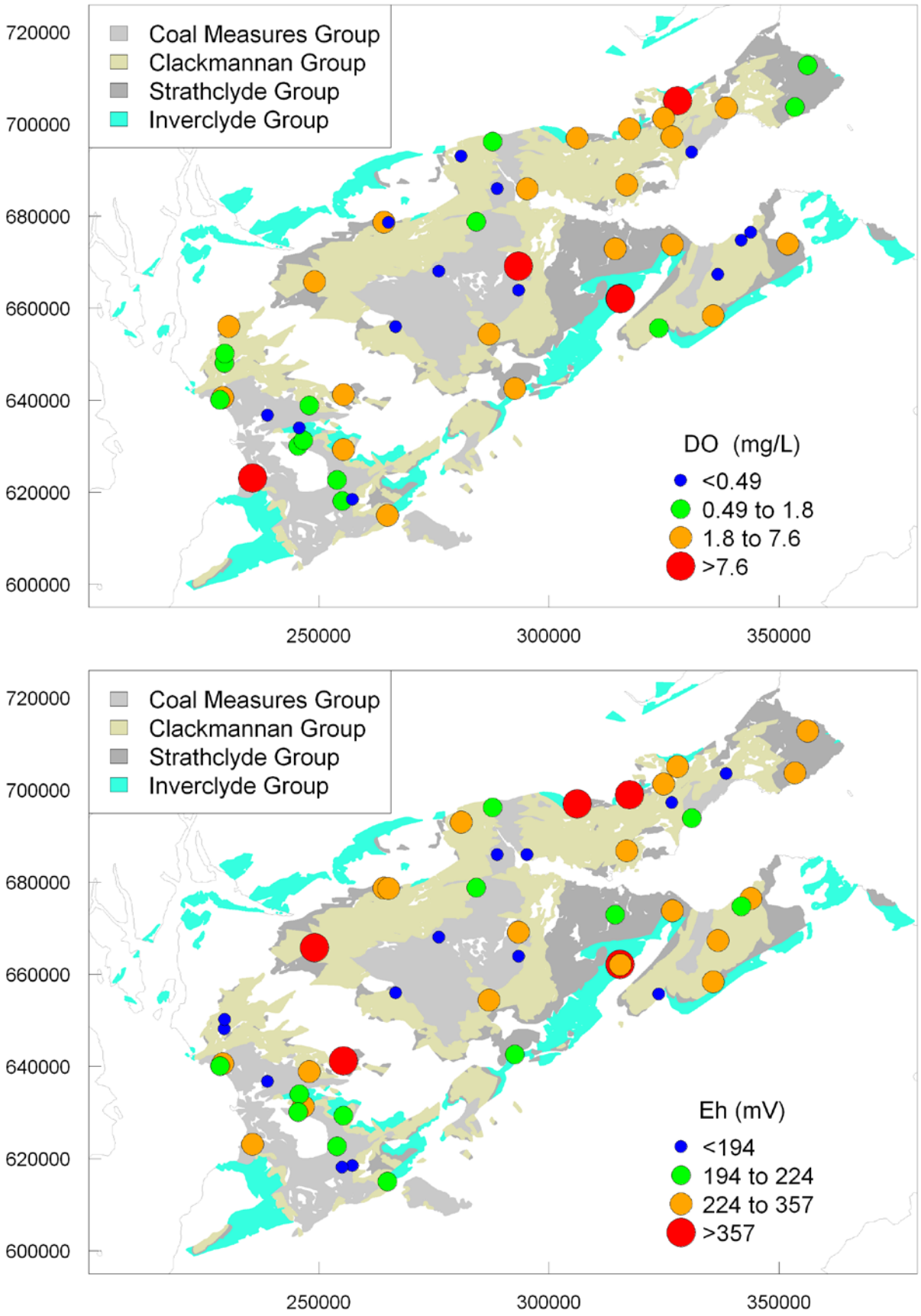


Figure 13 Maps showing the spatial distribution of dissolved oxygen (DO) and redox potential (Eh) in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

4.3 MAJOR IONS

The groundwaters show a large range of solute concentrations, with sample total dissolved solids (TDS) values in the range 65–19,000 mg/L (10^{th}–90^{th} percentile range 274–1620 mg/L, median 555 mg/L). The sample with the lowest TDS value is a spring water (Sample 41; Section 4.2.1). The highest TDS observed was in reducing groundwater from a deep borehole (>1000 m) in the Coal Measures (Sample 38).

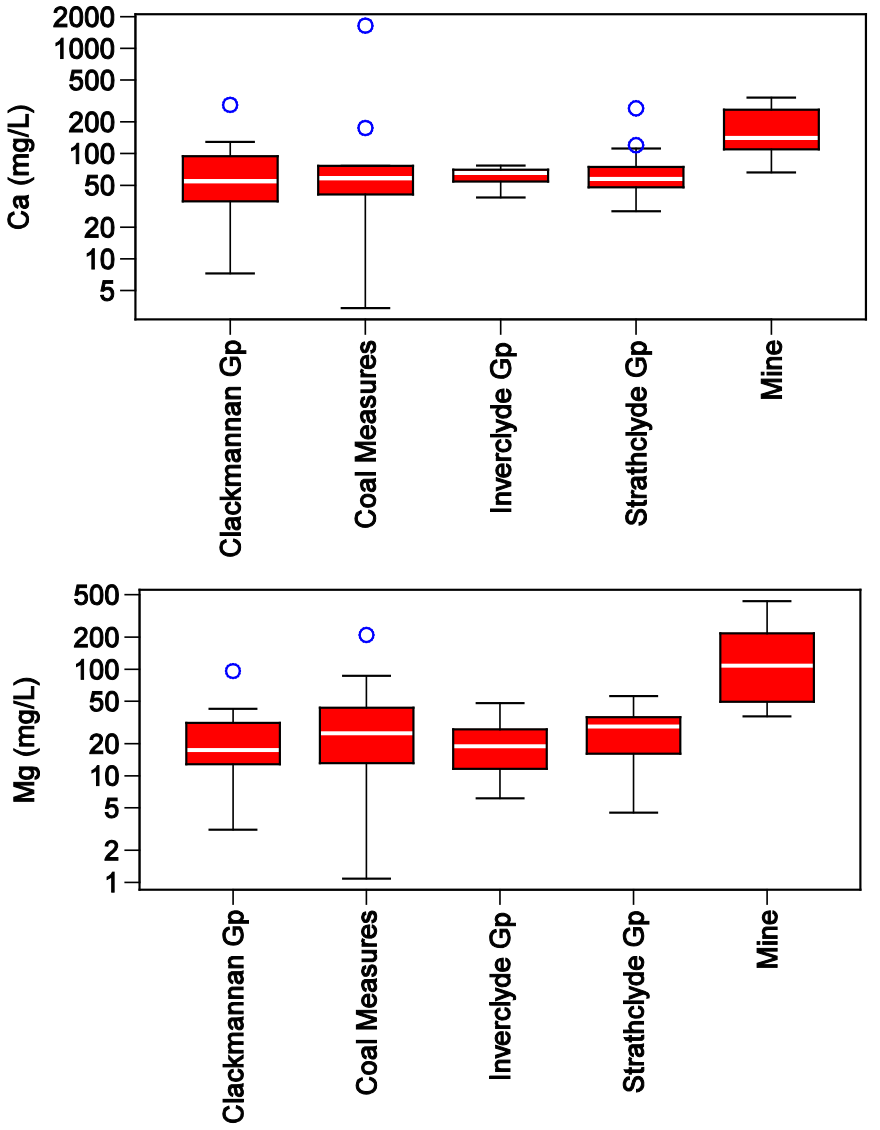
Ranges and distributions of the major cations Ca, Mg, Na and K are illustrated in box plots and maps in Figures 14 to 17. Ranges and distributions of the major anions Cl, SO_4 and NO_3-N are illustrated in box plots and maps in Figures 19 to 22. Major ion distribution is also illustrated in a Piper diagram (Figure 48). Water types encompass a large range from Ca-HCO_3, through Ca-Mg-HCO_3, through SO_4-rich types, Na-HCO_3, and (rarely) Na-Cl. Spatial variability of the major cations is correspondingly high.

Highest concentrations of Ca and Mg are found in the 'Mine' waters and some Coal Measures waters (Figure 14), probably due to reaction of carbonate minerals, and clays, which could have been enhanced by the generation of acid during the oxidation of pyrite. The lowest Ca concentration (3.4 mg/L) is from a Na-HCO_3 water in the Coal Measures, which has been subject to considerable ion exchange of Na (Sample 46). The low-TDS shallow spring water from the Clackmannan Group also has low Ca and Mg concentrations (Sample 41).

Concentrations of Na are also often high, particularly in groundwaters from the Coal Measures, 'Mine' waters and Clackmannan Group (Figure 16). The highest observed concentration, 5360 mg/L, occurs in the sample from the deepest source (~1000 m), from the Coal Measures Group (Sample 38).

Concentrations of K are also correspondingly high, with the extreme of 92 mg/L also from the deepest Coal Measures groundwater (Sample 38).

The high concentrations of dissolved cations are likely to reflect the effects of extreme water-rock interaction, in some cases (particularly deep boreholes) involving long residence times in the aquifers concerned. Sodium is probably largely sourced from dissolution of silicate minerals and ion-exchange reactions, the latter induced by young shallow groundwater mixing with older, more mineralised water. In some coastal areas, saline intrusion may also contribute to increased major ion concentrations. Sample 46, from the Ayrshire coast, has a high pH of 8.99 (Section 4.2.1) and a Na concentration of 259 mg/L. Although its Cl concentration is also slightly high, at 62.9 mg/L, the Na/Cl ratio of the sample is much higher than would be expected from simple seawater mixing. The elevated Na is, therefore, more likely to be caused by water-rock interaction (silicate dissolution and ion exchange) than sea water intrusion.



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

Figure 14 Box plots showing the distribution of calcium and magnesium concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

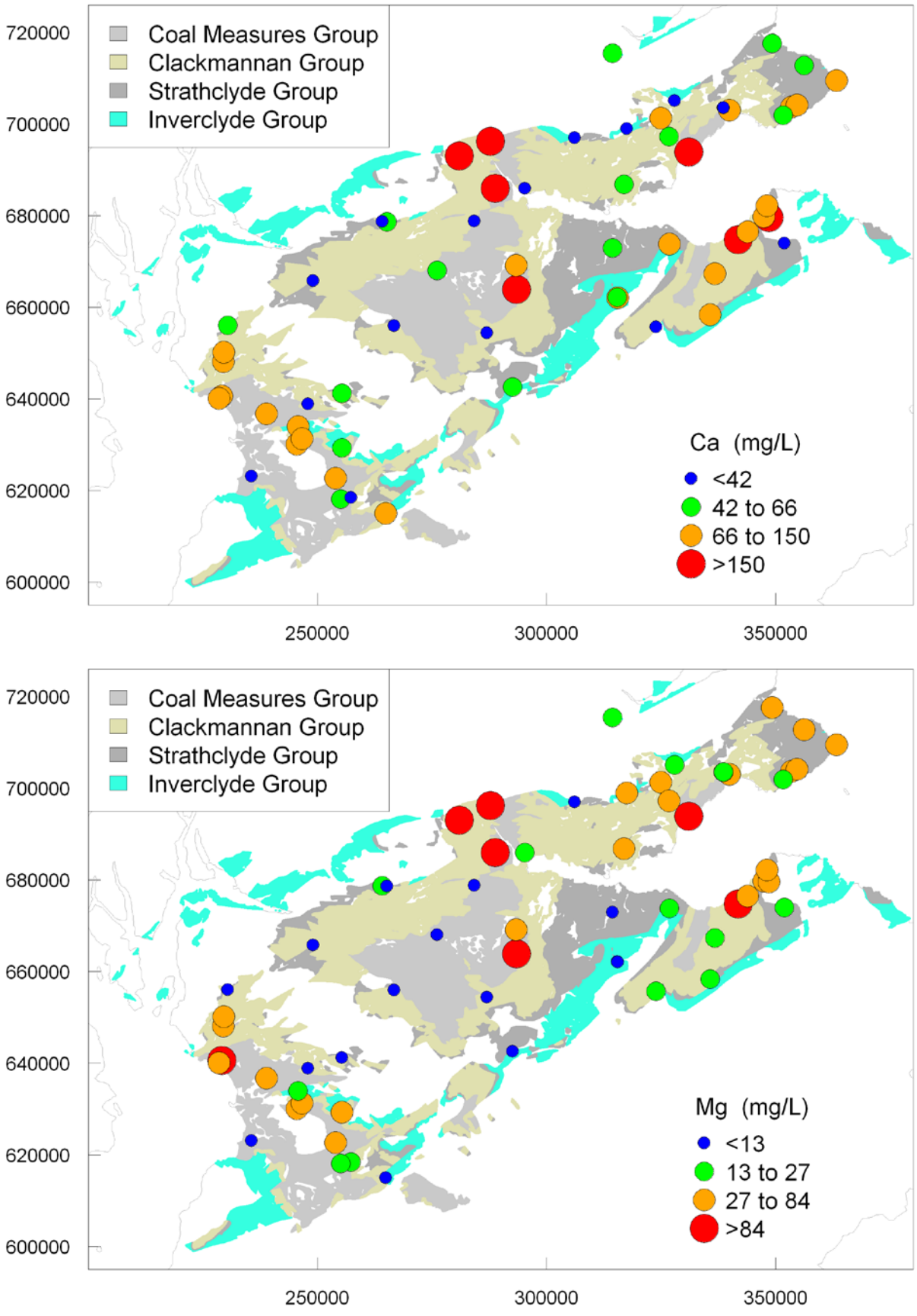
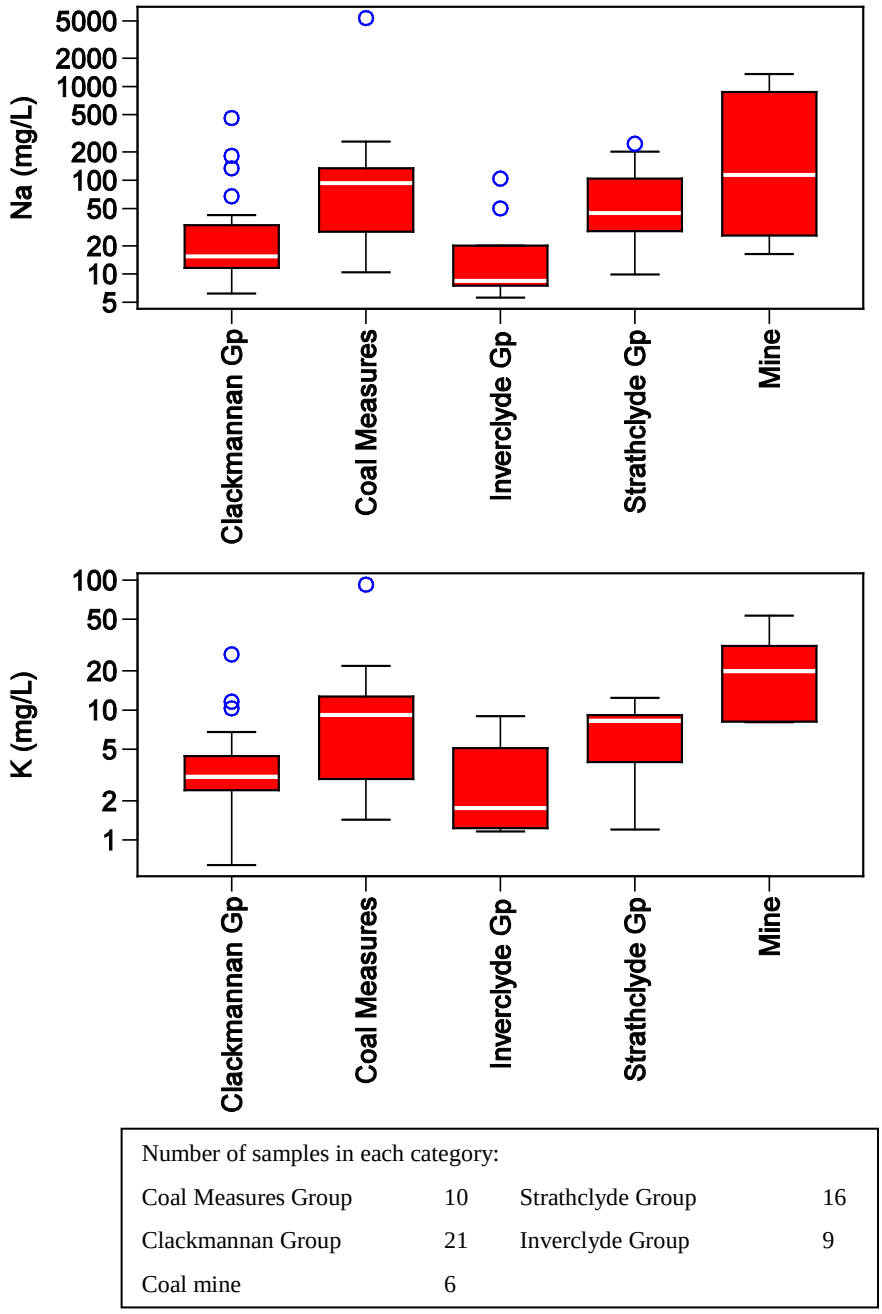


Figure 15 Maps showing the distribution of calcium and magnesium concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

Figure 16 Box plots showing the distribution of sodium and potassium concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

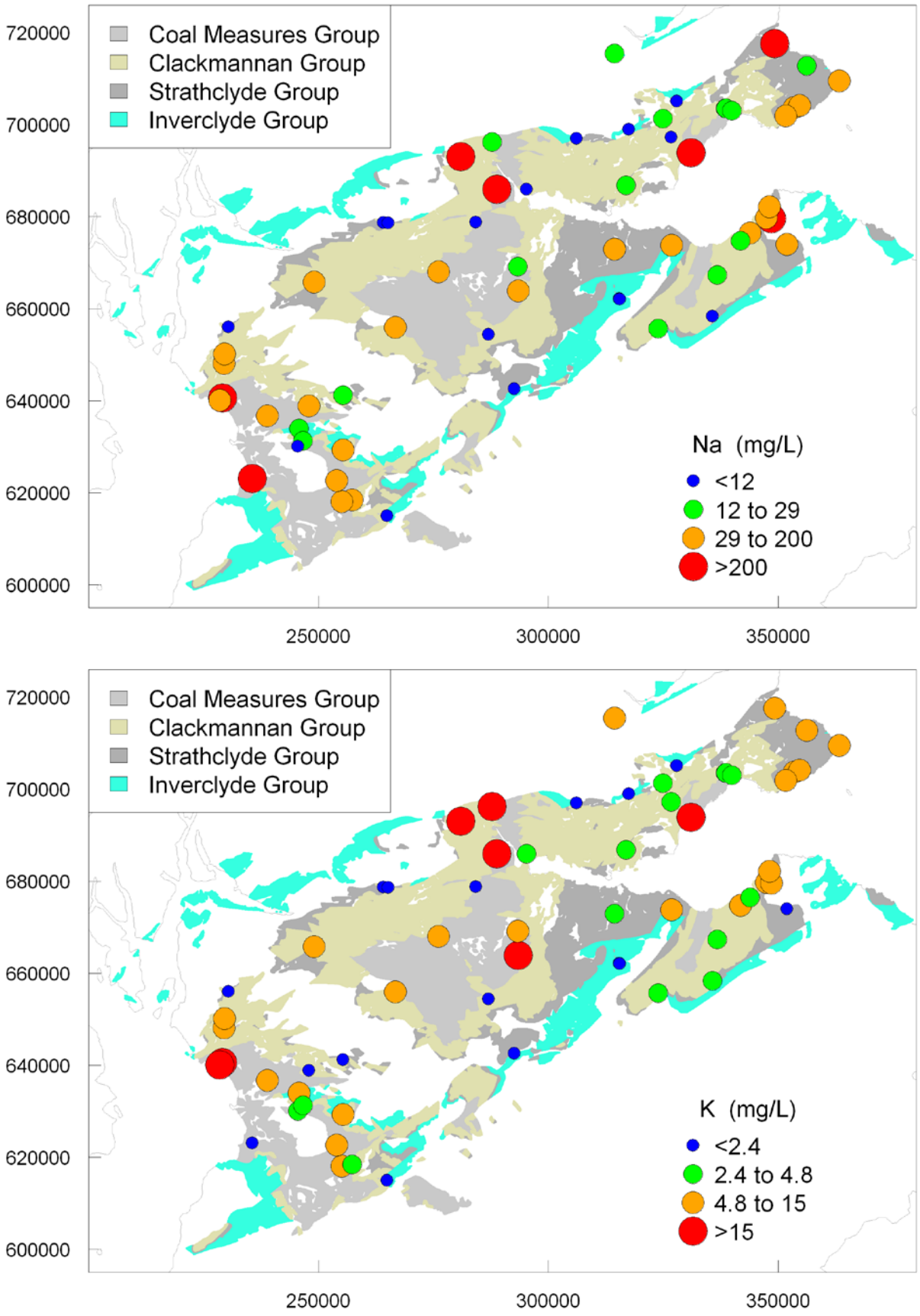


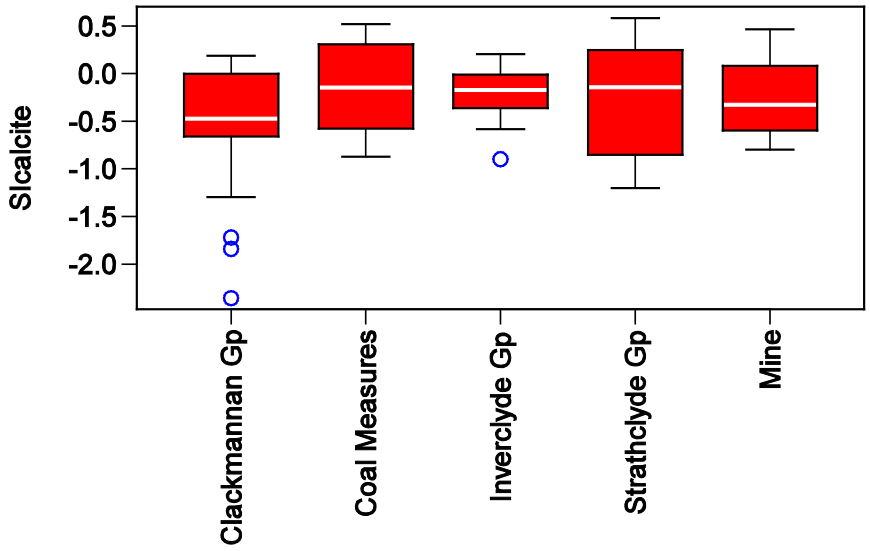
Figure 17 Maps showing the distribution of sodium and potassium concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

The groundwaters have variable calcite saturation indices (Figure 18) but in many cases are close to saturation, indicating both the presence of, and reaction with, carbonate minerals in the aquifers. The groundwaters with the most consistently undersaturated compositions are those from the Clackmannan Group.

Concentrations of Cl are typically high (Figure 19, Figure 20), but with a wide range from 5 to 11,500 mg/L.

The most saline sample analysed is from the deepest borehole sampled, in the Coal Measures Group (Sample 38). For reference, the Cl concentration in this sample is some 60% of seawater Cl concentration. The borehole is not obviously at risk of saline intrusion. Stable isotopic ratios ($\delta^{18}O$ -7.2 ‰, $\delta^{2}H$ -44.4 ‰) are also not consistent with a modern seawater origin, which would by definition be expected to be closer to 0 ‰. The sample is most likely to represent a long residence time groundwater which has undergone extensive reaction with the aquifer matrix, or mixing with connate water.

The spatial distribution of Cl (Figure 20) indicates some relatively high concentrations in groundwaters from coastal areas, which may indicate the influence of sea water, either directly as sea water intrusion, or from aerosols.



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

Figure 18 Box plot showing the distribution of calculated calcite saturation indices ($SI_{calcite}$) in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

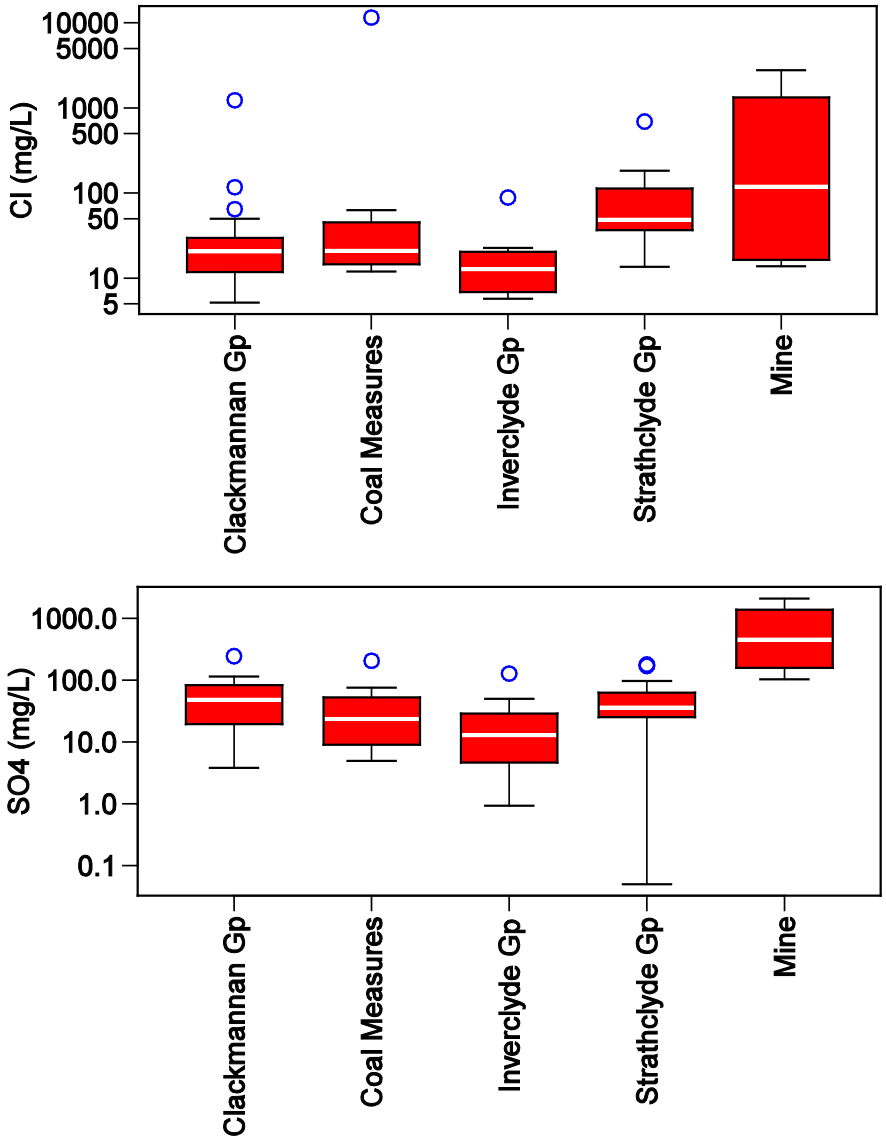


Figure 19 Box plots showing the distribution of chloride and sulphate concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

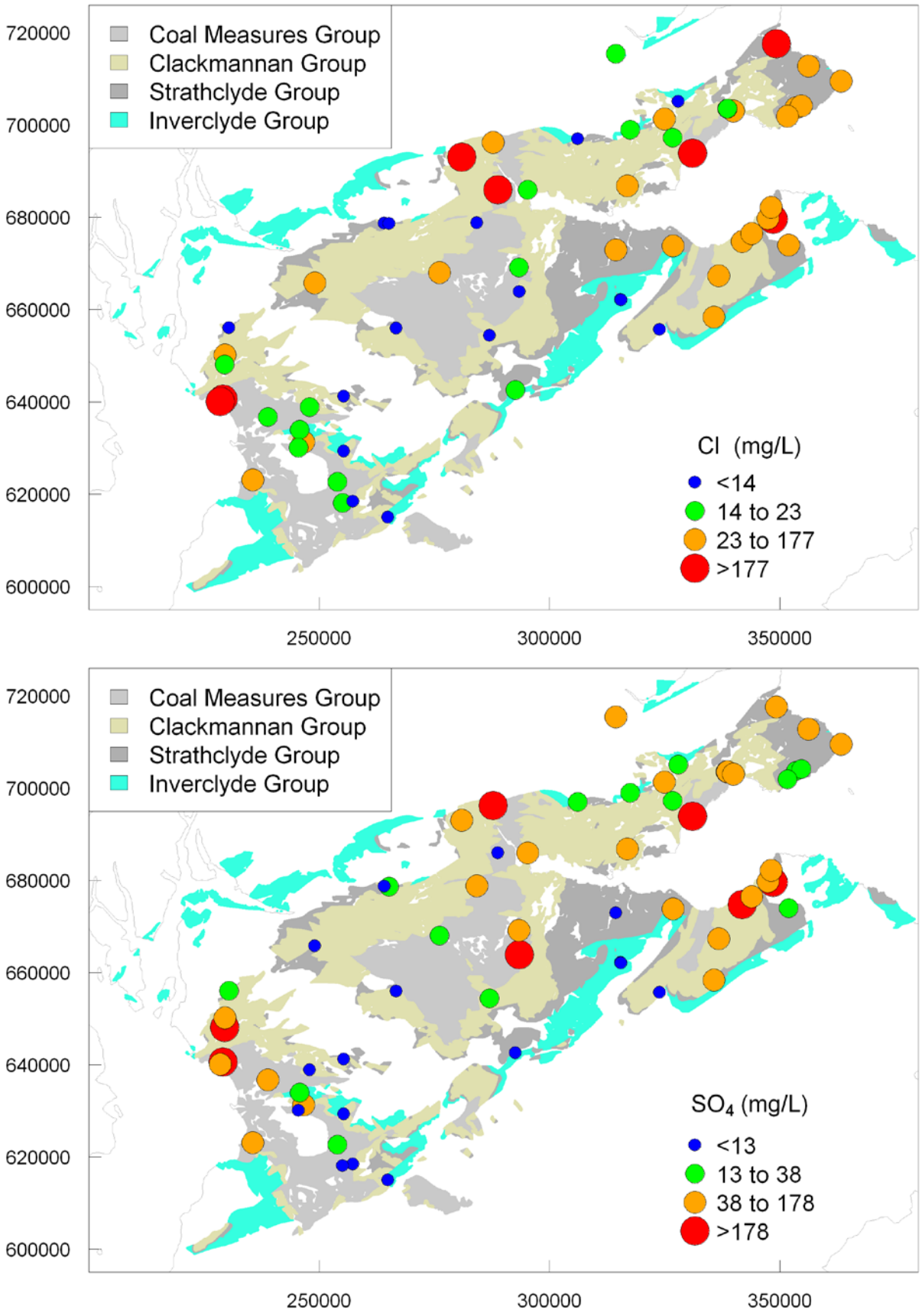


Figure 20 Maps showing the distribution of chloride and sulphate concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

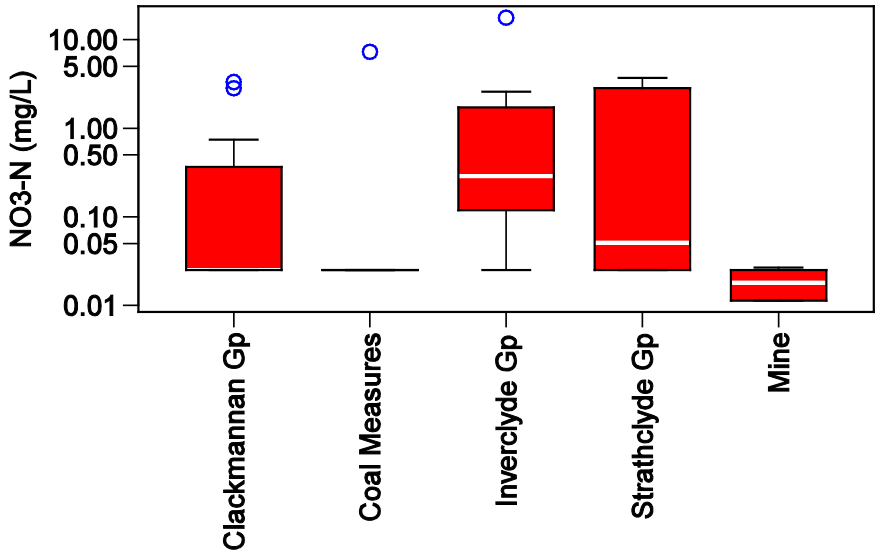
Concentrations of SO_4 span some five orders of magnitude (Figure 19), from <0.1 to 2100 mg/L (10^{th}–90^{th} percentile range 4.7–179 mg/L). The overwhelmingly dominant processes controlling this large range are likely to be oxidation of sulphide minerals, particularly in mining-impacted waters; and sulphate reduction in the most reducing conditions. Supporting this, the consistently highest concentrations are found in the 'Mine' waters (Figure 19), which in all cases have concentrations of >100 mg/L. Low concentrations (<5 mg/L SO_4) are usually associated with low NO_3-N concentrations and often high NH_4-N; all samples recorded in the field as having a smell of H_2S had SO_4 concentrations <5 mg/L. This indicates that sulphate reduction is a strong influence. Interestingly, the lowest SO_4 concentration was found in a sample from the sedimentary Strathclyde Group (Sample 23), which from other parameters appears to be a less strongly reducing aquifer.

Large variations in the concentrations of NO_3-N (Figure 21) also show the strong control that redox conditions have on the groundwater chemistry. Most concentrations were low, with 61% below detection limit. The largest ranges and highest median concentrations are found in groundwaters from the Inverclyde and Strathclyde groups. One sample had an unusually high concentration (17.7 mg/L) (Sample 33). This was from a farm borehole in the Inverclyde Group and is most likely to reflect contamination from an agricultural source. Groundwaters from the Clackmannan Group also show a large range, but with a low median value. Concentrations in groundwaters from the Coal Measures Group and 'Mine' waters are usually low, with one exception (Sample 49). The distributions suggest that denitrification – which occurs under reducing conditions – has been important in many of the groundwaters, and support the evidence from other redox-sensitive parameters that groundwaters from the Coal Measures Group and 'Mine' waters represent the most strongly reducing groups. NO_3-N concentrations plotted against land use type (Figure 22) indicate that the highest concentrations are generally found in areas of mixed cultivated land. However, the relationships with land use are poor, and concentrations are dominated by the redox conditions in the groundwater.

Other N species (NO_2-N and NH_4-N) show variability consistent with the reduction of nitrate under reducing conditions. Although 78% of analyses of NO_2-N were below the analytical detection limit, concentrations above 0.01 mg/L were in all cases found in groundwaters with low concentrations (<1 mg/L) of NO_3-N. Nitrite is a recognised intermediate product in the denitrification of NO_3.

Concentrations of NH_4-N are high in a number of samples, in several exceeding 1 mg/L. The maximum observed value is 2.6 mg/L in a sample of 'Mine' water (Sample 57). No value could be obtained for NH_4-N in the strongly reducing sample from a deep borehole in the Coal Measures mentioned earlier (Section 4.3) because of analytical problems caused by the high TDS concentration of the sample. By comparison with the chemistry of other samples in the study, the NH_4-N concentration is, however, likely to be high. The high NH_4 concentrations observed are consistent with degradation of natural organic matter in the aquifers.

High concentrations of dissolved organic carbon (DOC) (up to 70.8 mg/L) in a few samples are also indicative of the reducing – often strongly reducing – nature of some of the groundwaters.



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

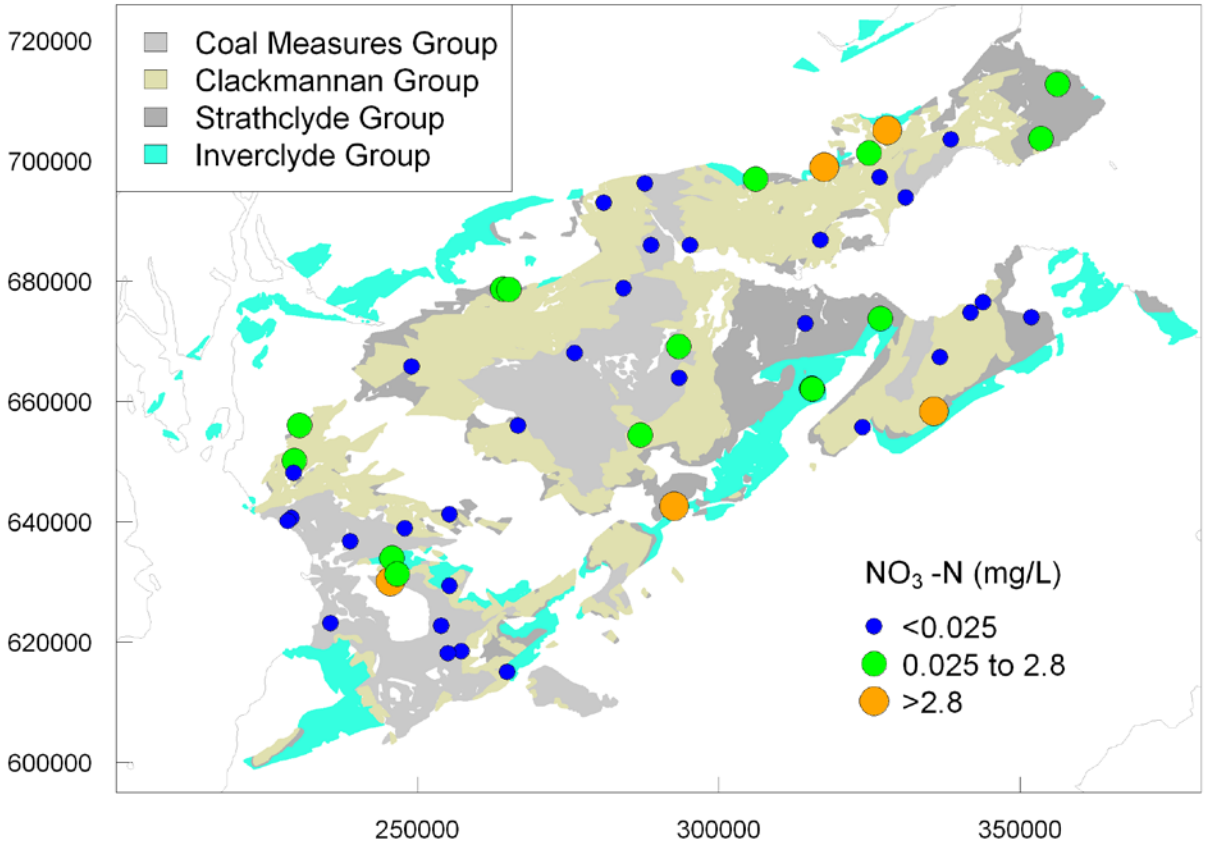
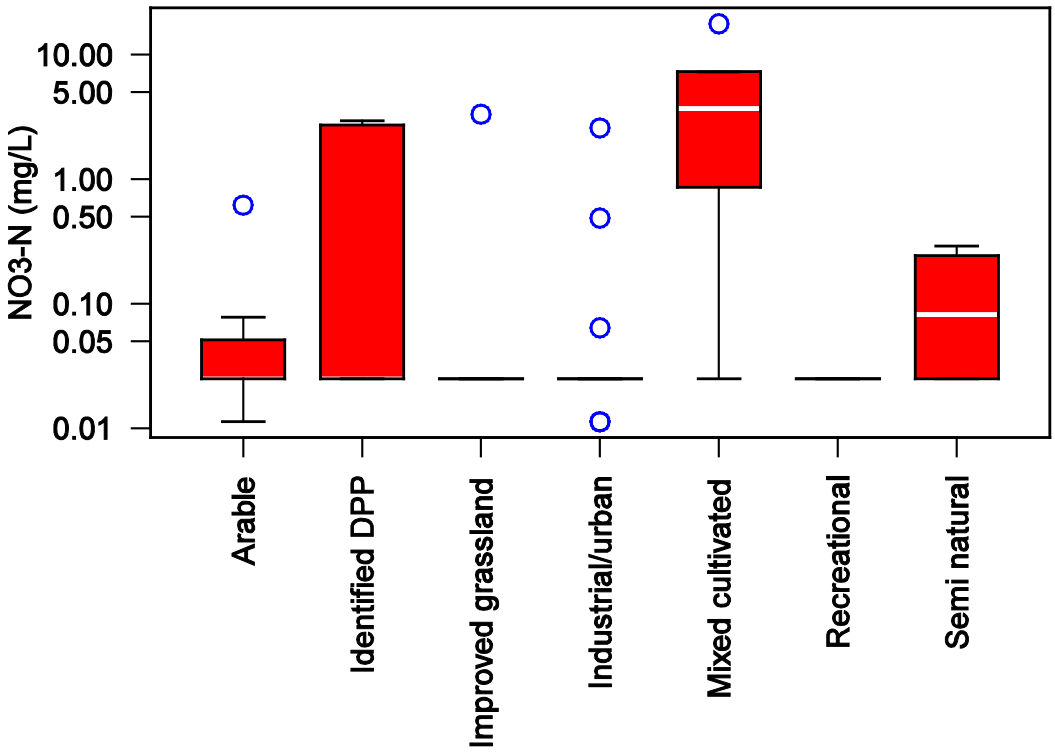


Figure 21 Box plot and map showing the distribution of nitrate concentrations (as NO_3-N) in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley



Number of analyses above detection limit in each category (numbers in brackets refer to total number of analyses, including those below detection):			
Arable	2 (7)	Industrial/urban	3 (13)
Identified DPP	4 (10)	Mixed cultivated	4 (5)
Improved grassland	1 (5)	Recreational	0 (2)

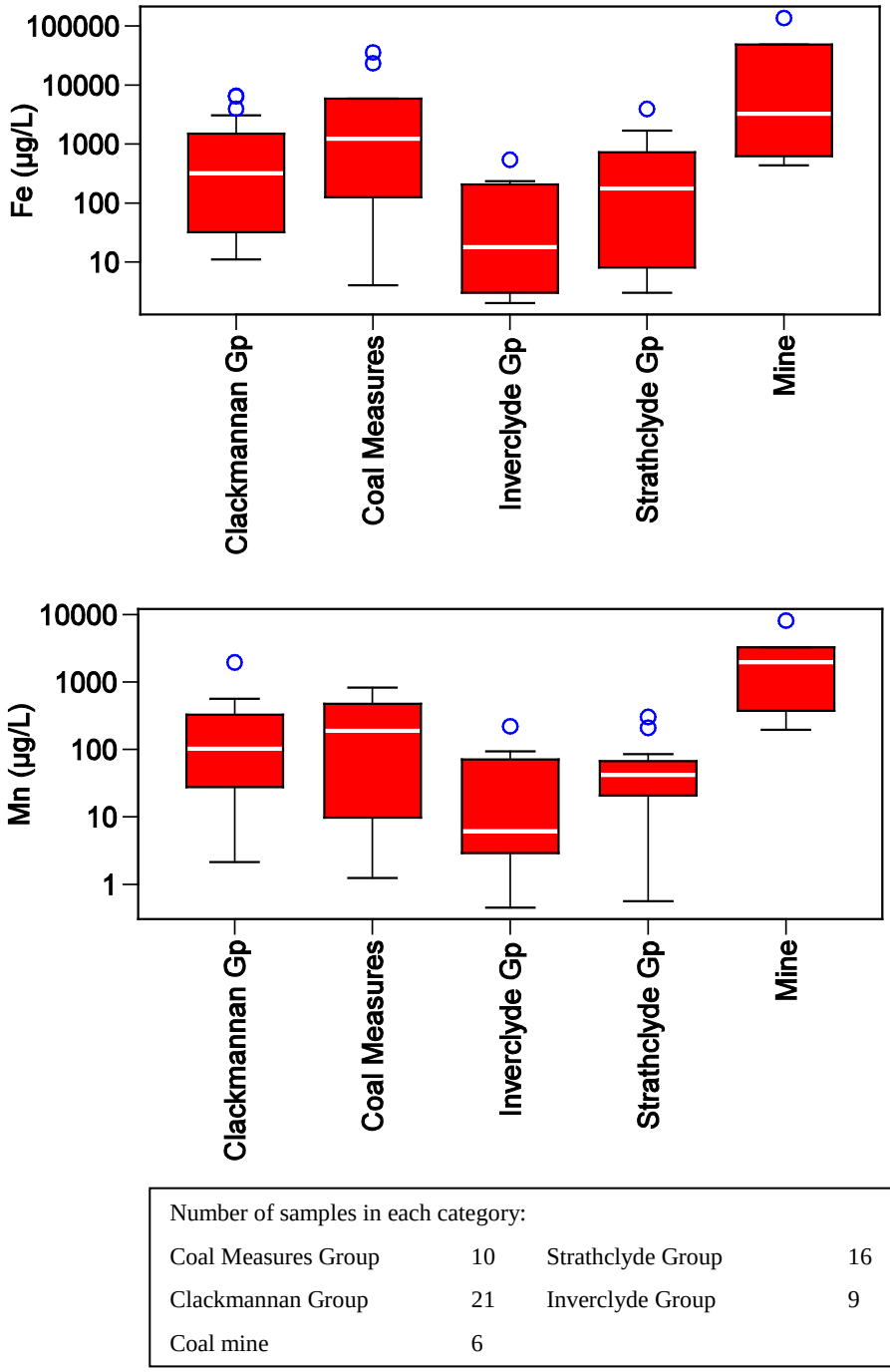
Figure 22 Variations in nitrate concentrations (in mg/L as NO_3-N) in groundwaters with land use class, based on land use maps and field observations of the 200 m surrounding the groundwater source. Identified DPP refers to improved grassland positively identified as being used for dairy, pigs and/or poultry. Nitrate concentrations are dominated by aquifer redox conditions rather than land use.

4.4 MINOR AND TRACE ELEMENTS

4.4.1 Iron and manganese

Concentrations of Fe and Mn show very large ranges, spanning five orders of magnitude (Figure 23), which is consistent with the large variations in redox status observed in the Carboniferous aquifers. The highest concentrations of Fe are found in groundwater from the Coal Measures Group and 'Mine' waters. Manganese concentrations are highest in the 'Mine' waters, with relatively high concentrations also in the Coal Measures and Clackmannan groups. Both elements are found at highest concentrations in groundwaters with low DO concentrations: Fe and Mn concentrations of >1 mg/L are found in waters with DO concentrations <2 mg/L. Dissolved Fe and Mn are most likely to be derived from reductive dissolution of their respective oxide mineral phases, together with oxidation of iron sulphide, particularly in carbonaceous horizons.

Maps of the distributions of Fe and Mn show that the highest concentrations are generally in the centre and northeast coalfield areas of the Midland Valley (Figure 24).



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

Figure 23 Box plots showing the distribution of iron and manganese concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

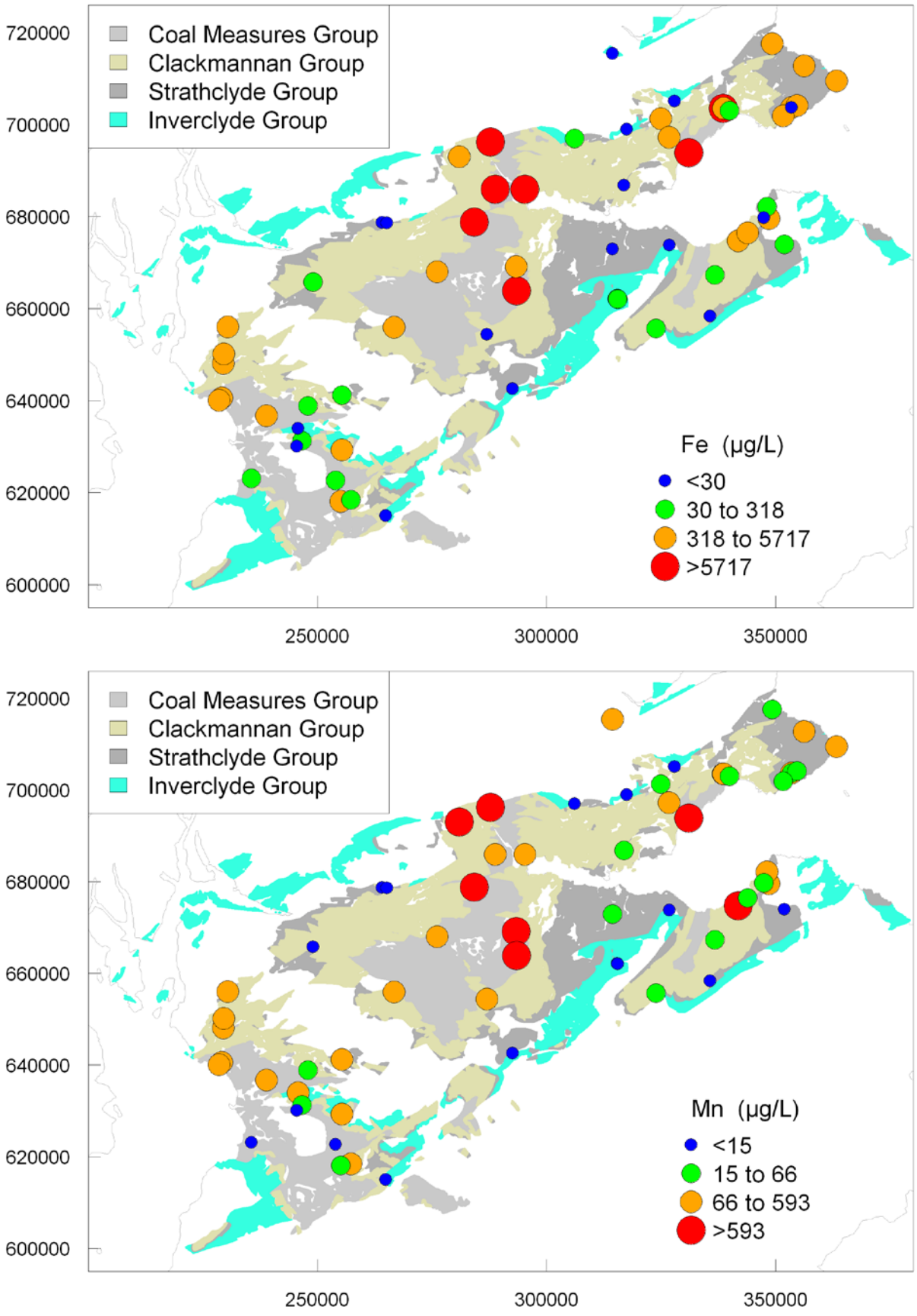


Figure 24 Maps showing the distribution of iron and manganese concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

4.4.2 Fluoride

Fluoride concentrations are mostly low (10^{th}–90^{th} percentile range 0.05–0.44 mg/L). The distribution is spatially heterogeneous and no consistent pattern is observed between aquifer units (Figure 25). Potential sources of F include phosphate minerals, detrital micas and fluorite in the aquifer sediments. All the samples are undersaturated with respect to fluorite.

4.4.3 Phosphorus

Concentrations of dissolved P are usually <50 µg/L (Figure 26), but reach a maximum of 432 µg/L. Some high outliers occur in the Coal Measures and Clackmannan groups. Likely sources include dissolution of phosphate minerals desorption from iron oxides under reducing conditions and degradation of organic matter, as well as agricultural pollution. The highest observed concentration was from the deepest borehole, >1000 m in the Coal Measures Group (Sample 38), where, although the dominant surrounding land use was arable agriculture, it is unlikely that agricultural pollution of the sampled groundwater has occurred (Figure 27). Pollution may be contributory in some cases, but many of the outlier P concentrations occur in the more reducing (and mine-impacted) groundwaters, which would also be consistent with a natural (mineral, organic matter) origin.

4.4.4 Iodine

Concentrations of I are variable but show no systematic difference between aquifer groups and no distinct spatial trends (Figure 28). Concentrations are relatively high in the saline water samples. Sources are likely to be organic matter and clays in the sediments.

4.4.5 Boron

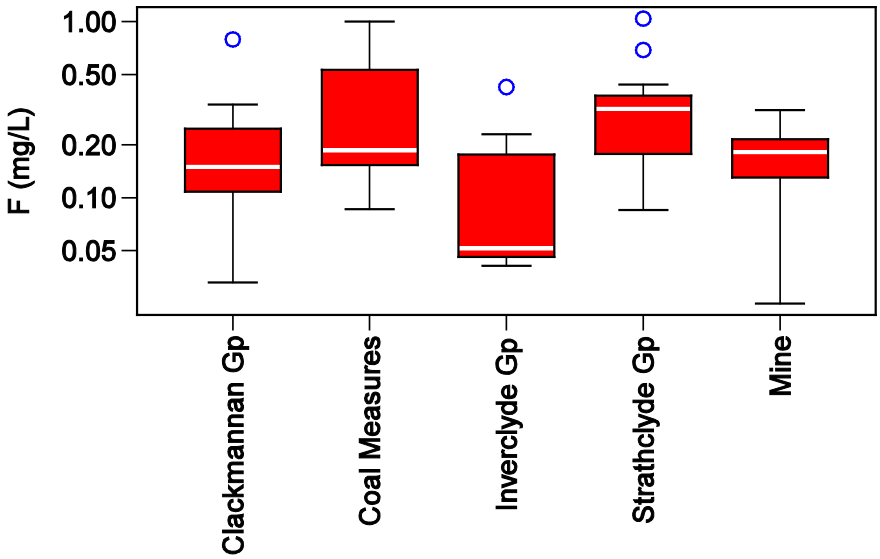
Concentrations of B have a 10^{th}–90^{th} percentile range of 14–334 µg/L (Figure 29). Concentrations are highest in samples alkalinities of more than 200 mg/L. Natural sources of B include seawater (in coastal areas) and clays (by dissolution and/or ion-exchange reaction). Boron concentrations plotted against land use indicate that some of the highest concentrations are found in industrial/urban areas (Figure 30). This suggests that urban pollution may be an additional factor.

4.4.6 Arsenic

Arsenic concentrations are in most cases low, in most samples <2 µg/L. Median concentrations for each of the aquifer groups are below 1 µg/L, but with some outliers up to 10.8 µg/L (Figure 31). The highest values are from waters in the Coal Measures Group. Pyrite oxidation is the most likely source of dissolved As in the study area. Since As is known to be strongly associated with sulphide minerals, it is perhaps surprising that concentrations are as low as observed. The distribution of As across the Midland Valley is somewhat variable but with a slight indication of higher concentrations in the west (Figure 31).

4.4.7 Uranium

Uranium concentrations are highly variable, with a 10^{th}–90^{th} percentile range of 0.009 to 4.5 µg/L, and little discernible difference between the aquifer groups (Figure 32). The highest concentrations in the Midland Valley are relatively high compared to groundwaters from England and Wales (Shand et al. 2007). The variability in U concentration reflects the varying redox status of the groundwaters: concentrations in reducing waters are expected to be low due to reduction of U to the tetravalent state and immobilisation by formation of UO_2 and incorporation into other minerals (e.g. calcite; Sturchio et al. 1998). Concentrations of U greater than 2 µg/L occur in groundwaters greater than *c.* 250 mg/L HCO_3 which suggests that U mobilisation is greatest in alkaline waters, with U-carbonate complexes being important solute species.



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

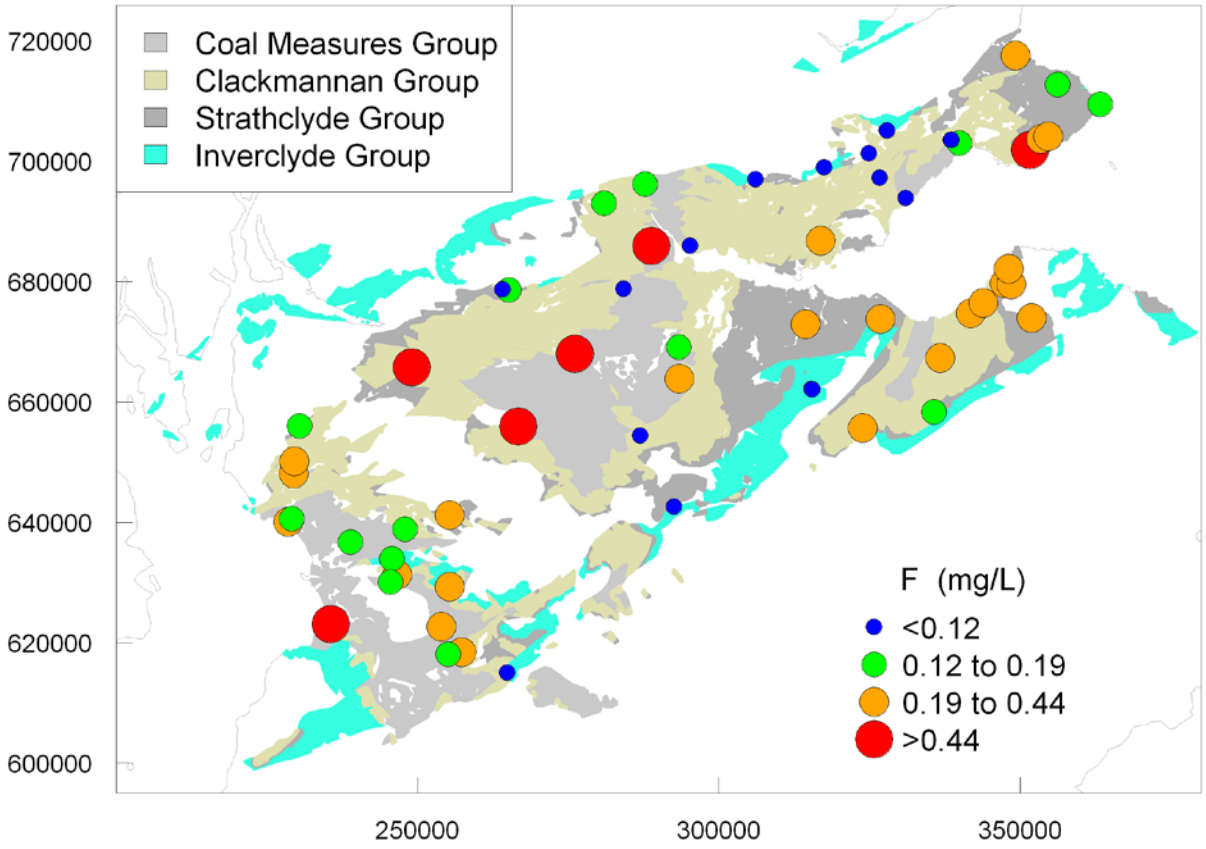
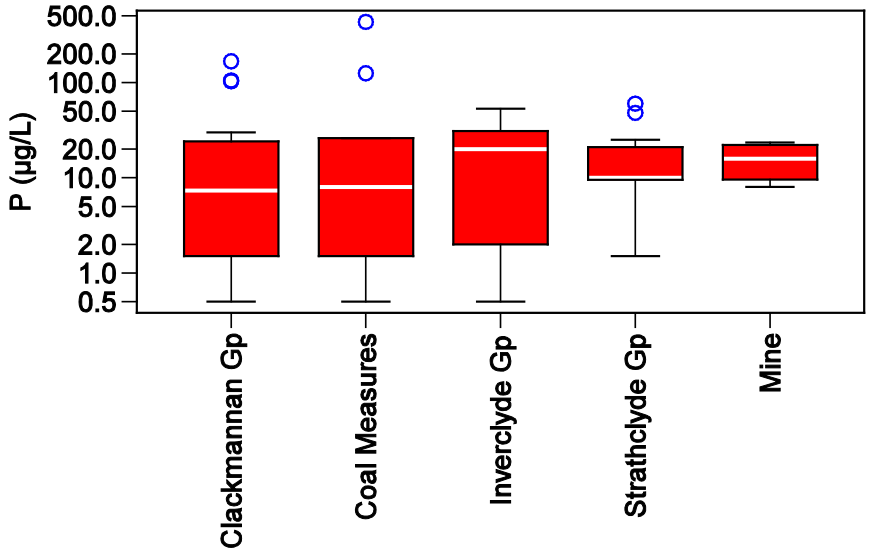


Figure 25 Box plot and map showing the distribution of fluoride concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	4		

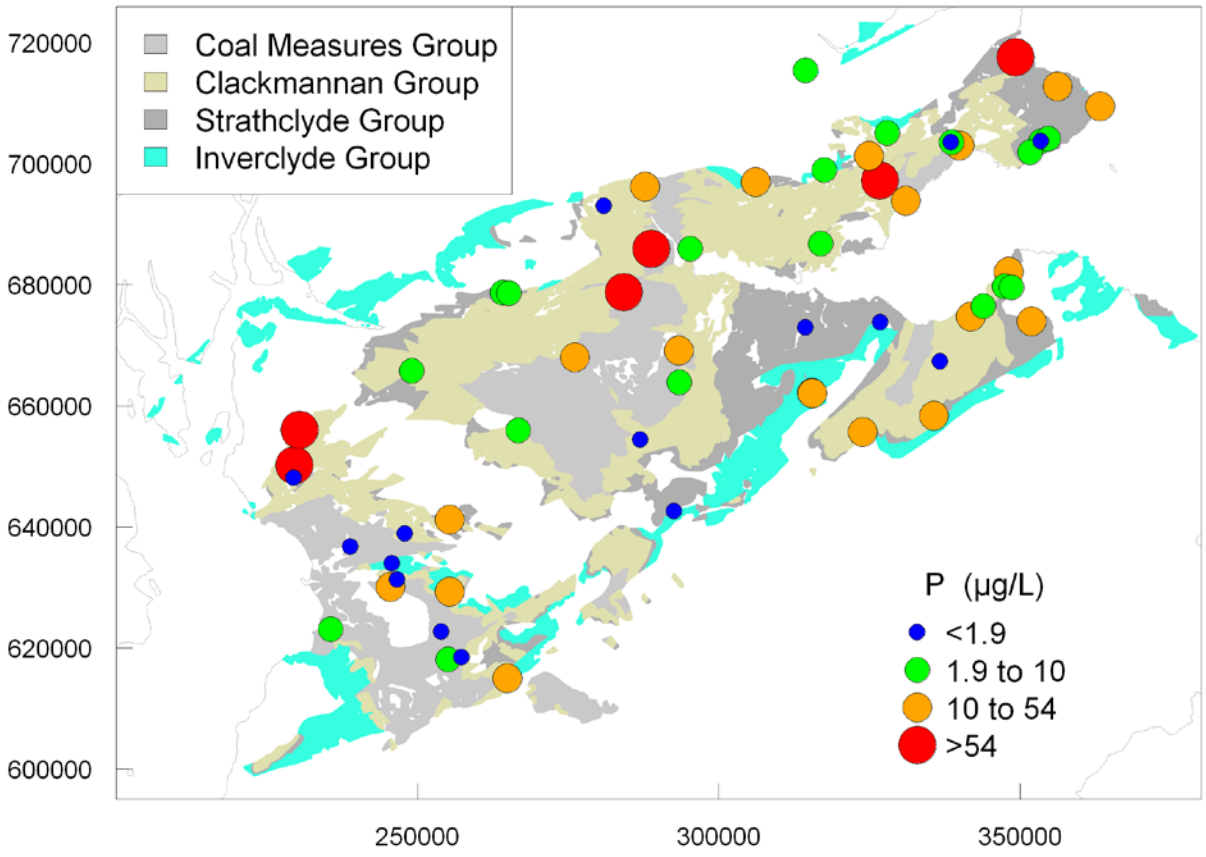
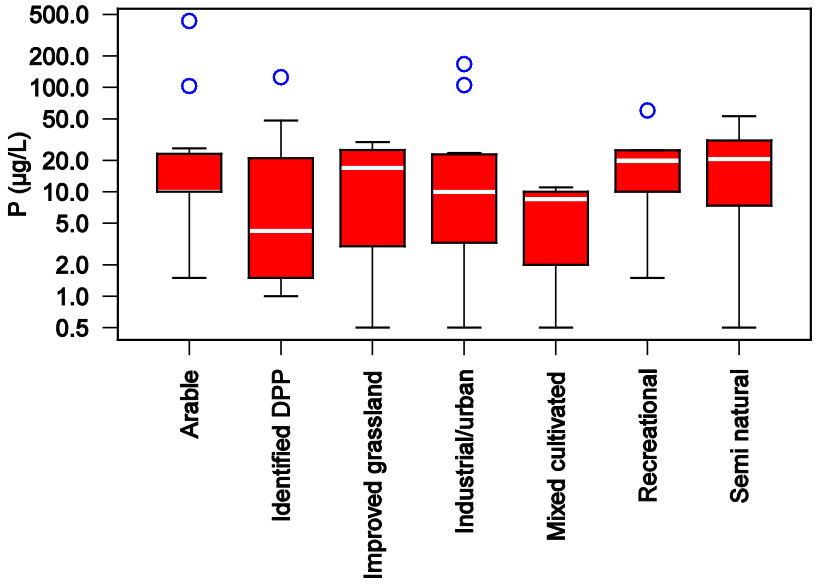


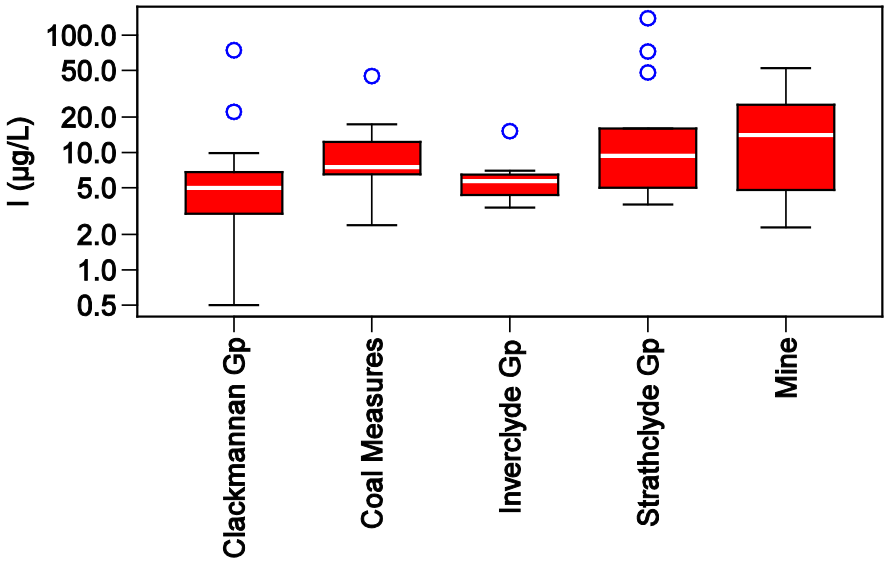
Figure 26 Box plot and map showing the distribution of P concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley



Number of analyses above detection limit in each category (numbers in brackets refer to total number of analyses, including those below detection):

Arable	5 (13)	Industrial/urban	7 (11)
Identified DPP	5 (10)	Mixed cultivated	2 (6)
Improved grassland	4 (6)	Recreational	3 (5)
Semi natural	8 (9)		

Figure 27 Variation in phosphorus concentrations (as µg P/L) in groundwater with land use type across the Midland Valley, based on land use maps and field observations of the 200 m diameter area around the groundwater source. Identified DPP refers to improved grassland positively identified as being used for dairy, pigs and/or poultry.



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

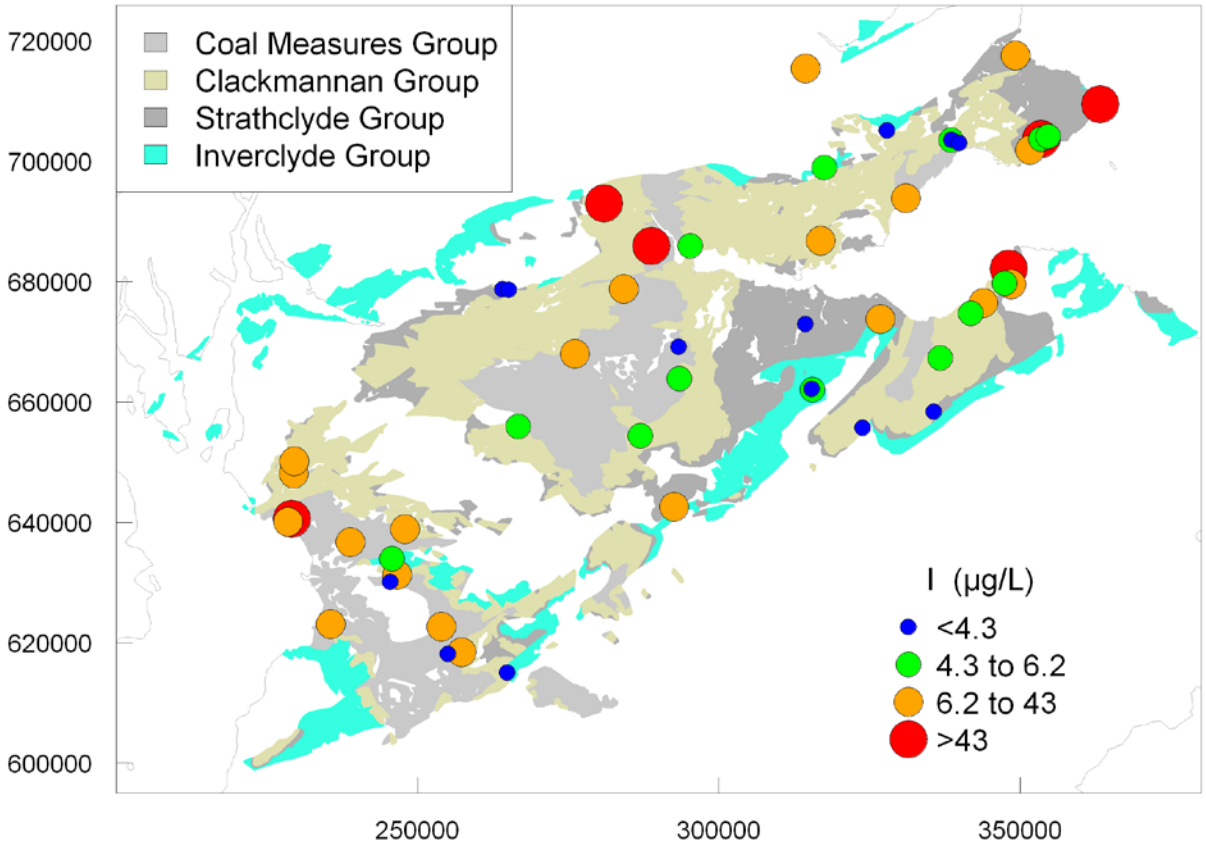
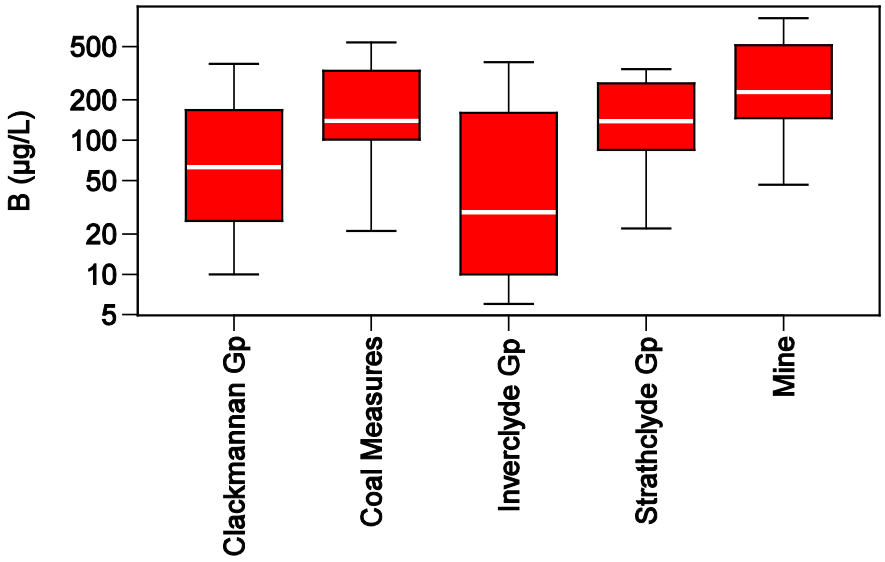


Figure 28 Box plot and map showing the distribution of iodine concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

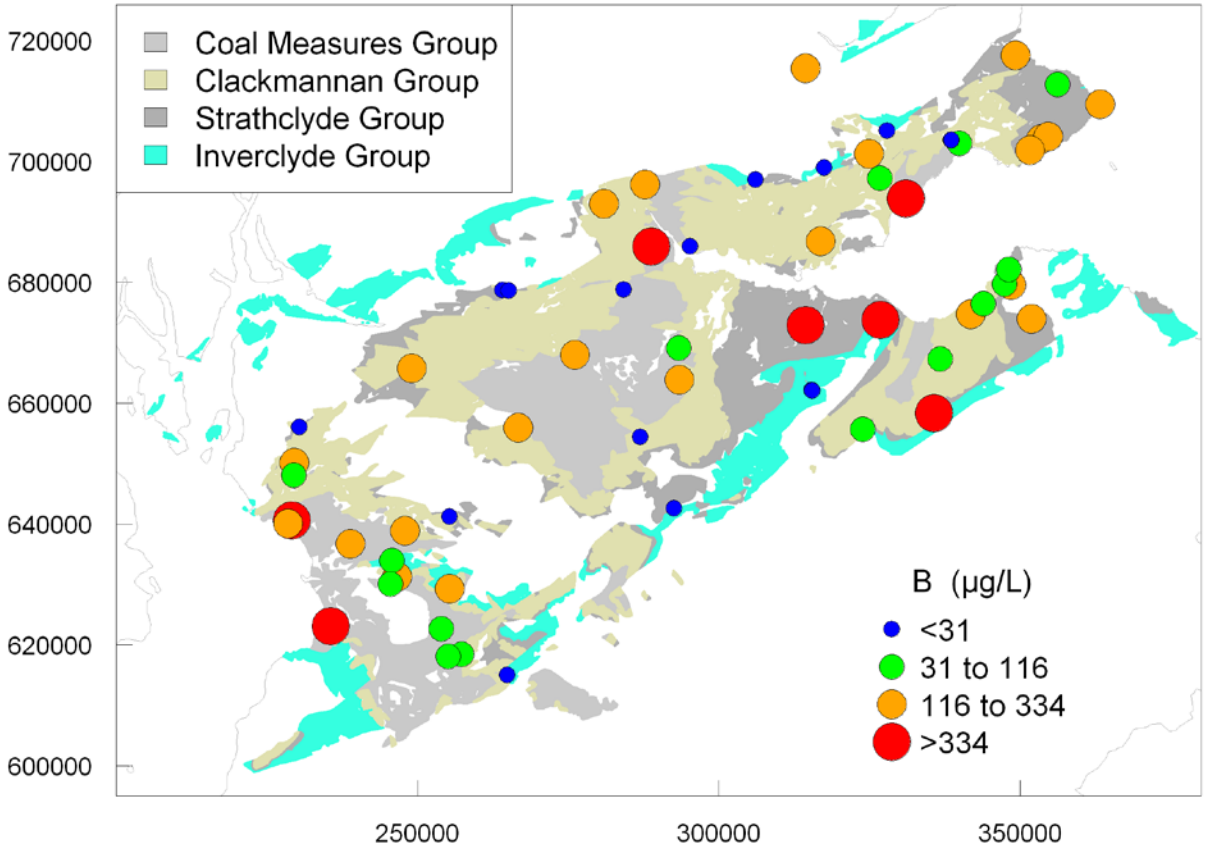


Figure 29 Box plot and map showing the distribution of boron concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

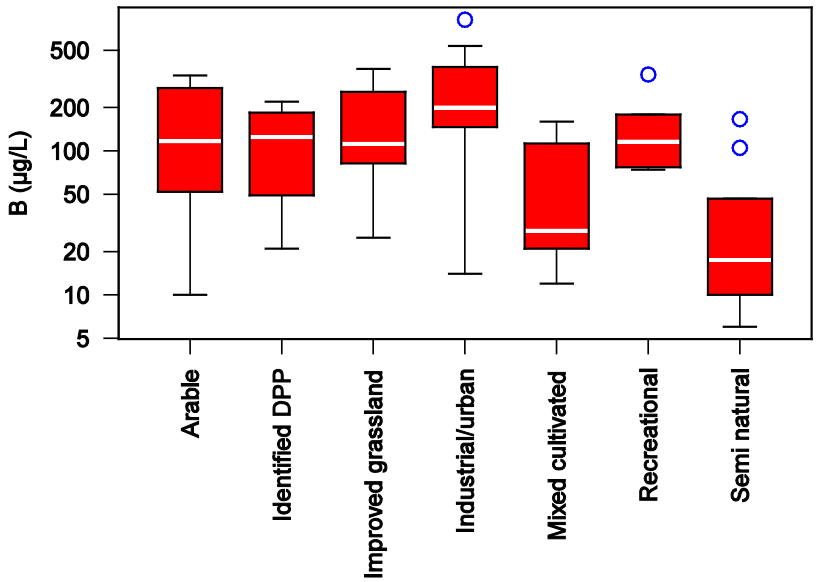
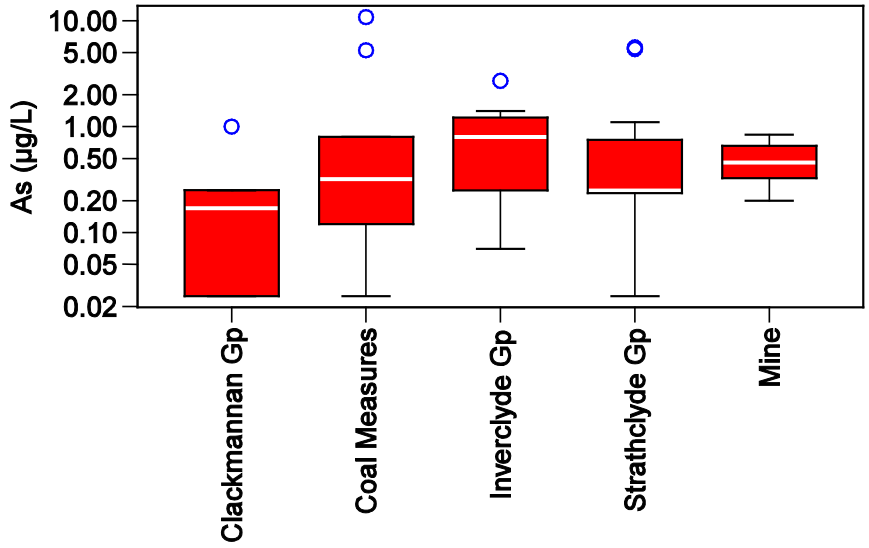


Figure 30 Box plot showing the distribution of boron in groundwaters with land use



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	4		

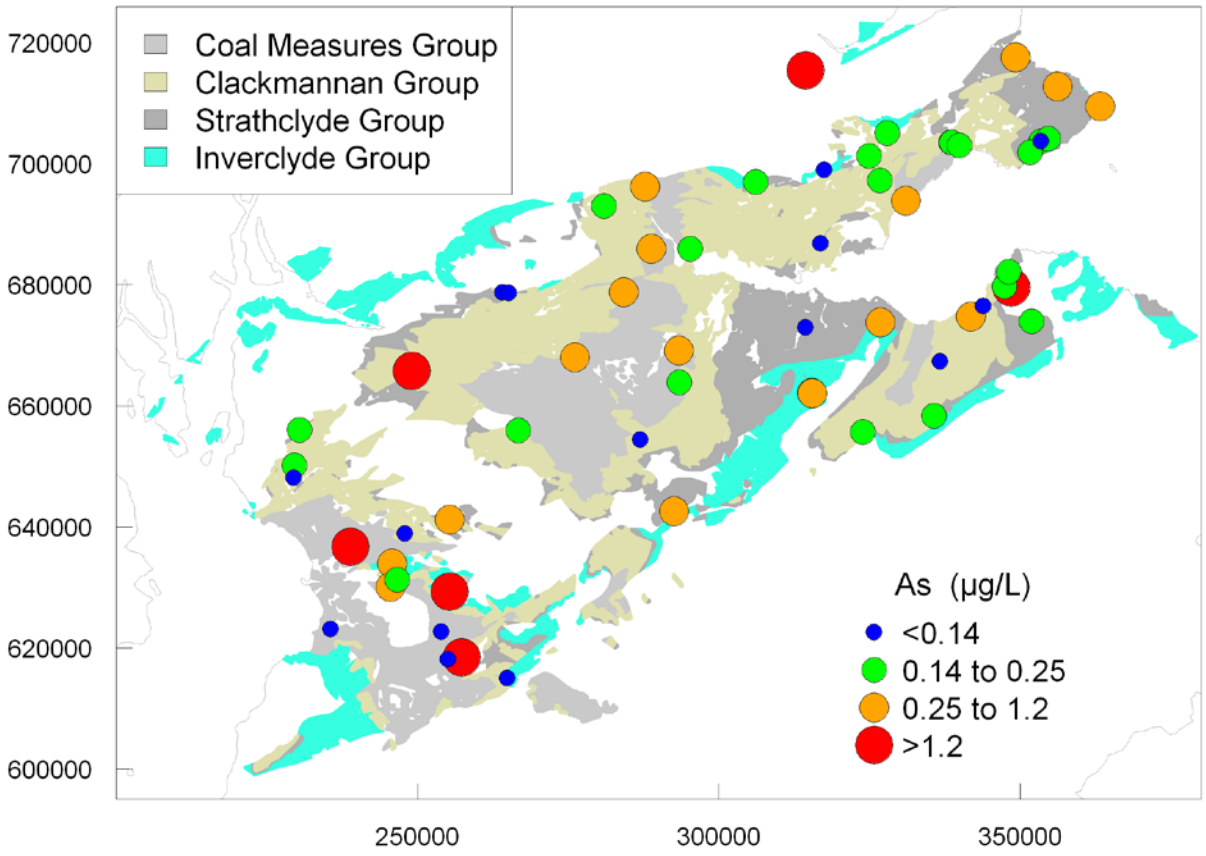
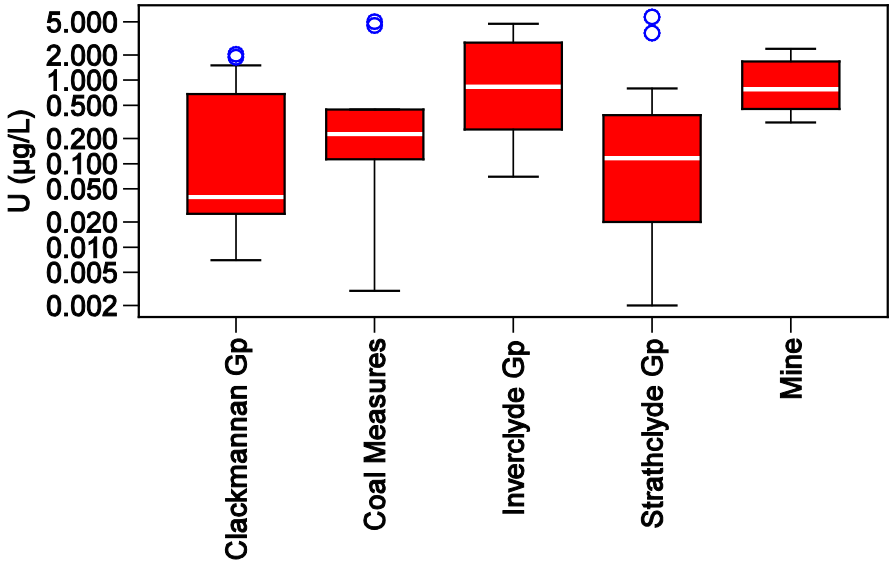


Figure 31 Box plot and map showing the distribution of arsenic concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

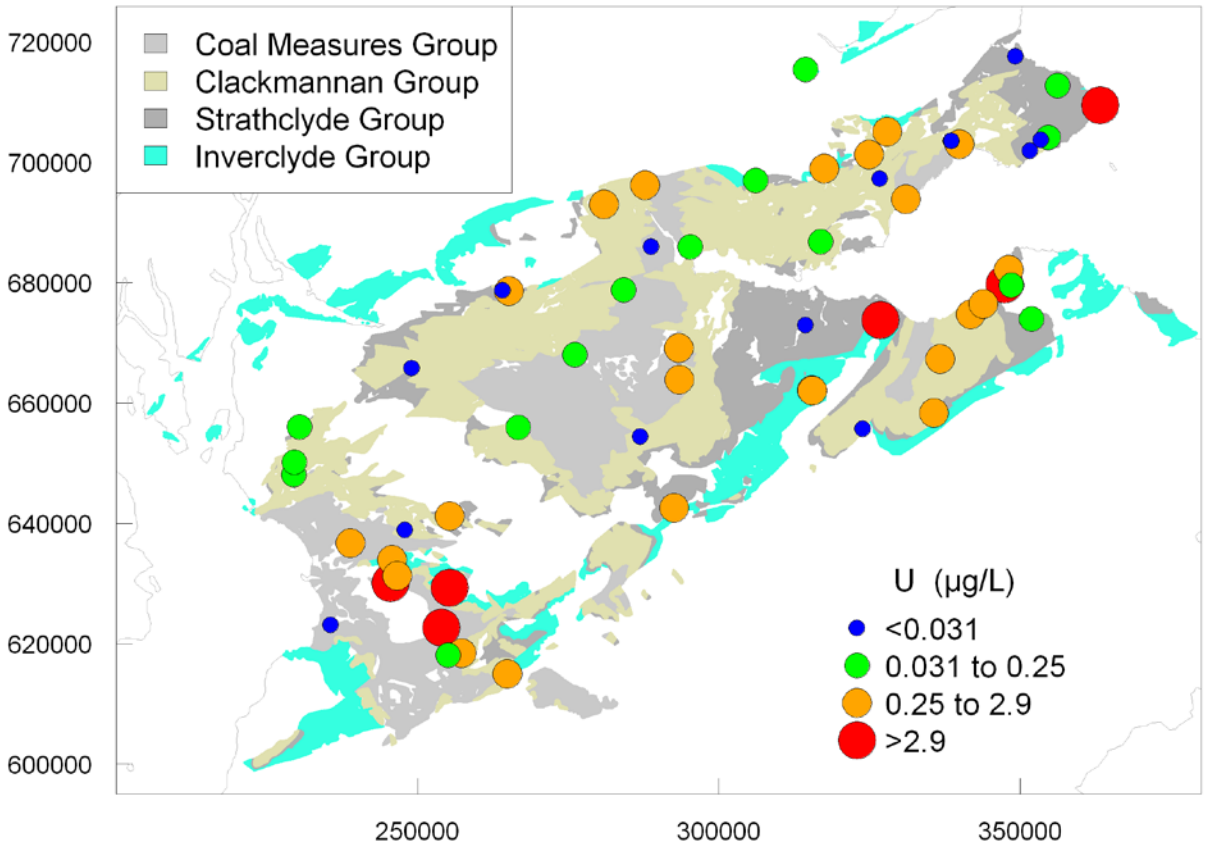


Figure 32 Box plot and map showing the distribution of uranium concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

4.4.8 Molybdenum

No distinct difference is apparent in Mo concentration between different aquifer groups, and the regional distribution is spatially variable (Figure 33). Concentrations in most groundwaters are <1 µg/L, although the highest observed concentration is 5 µg/L (Sample 31). The Mo present is likely to be largely derived from oxidising sulphide minerals. Waters with low SO_4

concentrations, indicative of sulphate reduction, tend to have low Mo concentrations, consistent with immobilisation of Mo in a sulphide mineral phase.

4.4.9 Copper

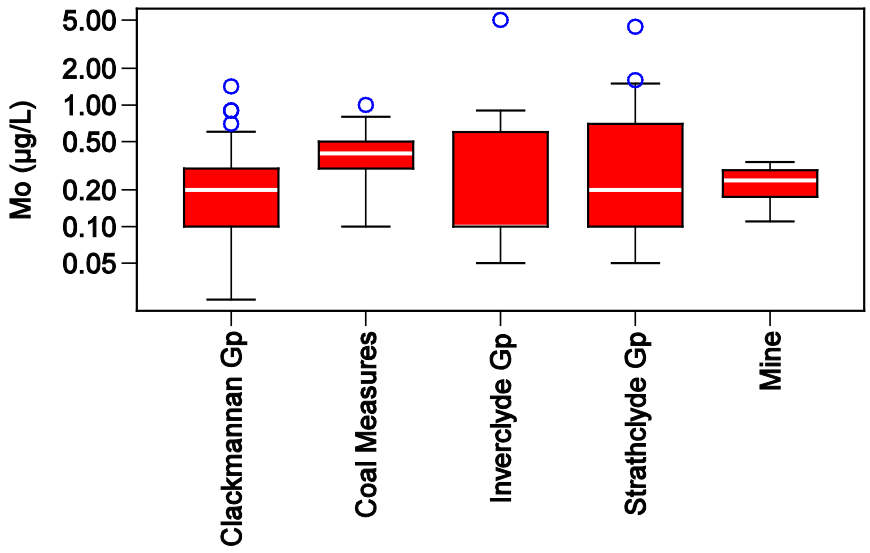
Concentrations of Cu are not high. The highest observed values are in groundwaters from the Inverclyde and Strathclyde groups (Figure 34), which tend to be more oxic. Interestingly, rather low concentrations occur in the 'Mine' waters, despite high concentrations of dissolved Fe and SO_4.

4.4.10 Nickel

Although most Ni concentrations are much less than 5 µg/L (Figure 35), the range is large, with a 10^{th}–90^{th} percentile range of 0.14 to 40 µg/L, and some outliers with very high concentrations. The maximum concentration in non-'Mine' waters is 43.1 µg/L. Groundwaters from the 'Mine' category have Ni concentrations which are consistently high compared to the other groups, with a maximum value of 94.9 µg/L. Regional distributions are variable with no clear pattern (Figure 35). Derivation of Ni from metal oxides and sulphide minerals is the most likely origin.

4.4.11 Zinc

Concentrations of Zn are also relatively high, the highest being in groundwaters from the Clackmannan and Strathclyde groups. The 10^{th}–90^{th} percentile range is 2.1–163 µg/L. The regional distribution indicates that concentrations are higher in the east of the region (Figure 36).



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	4		

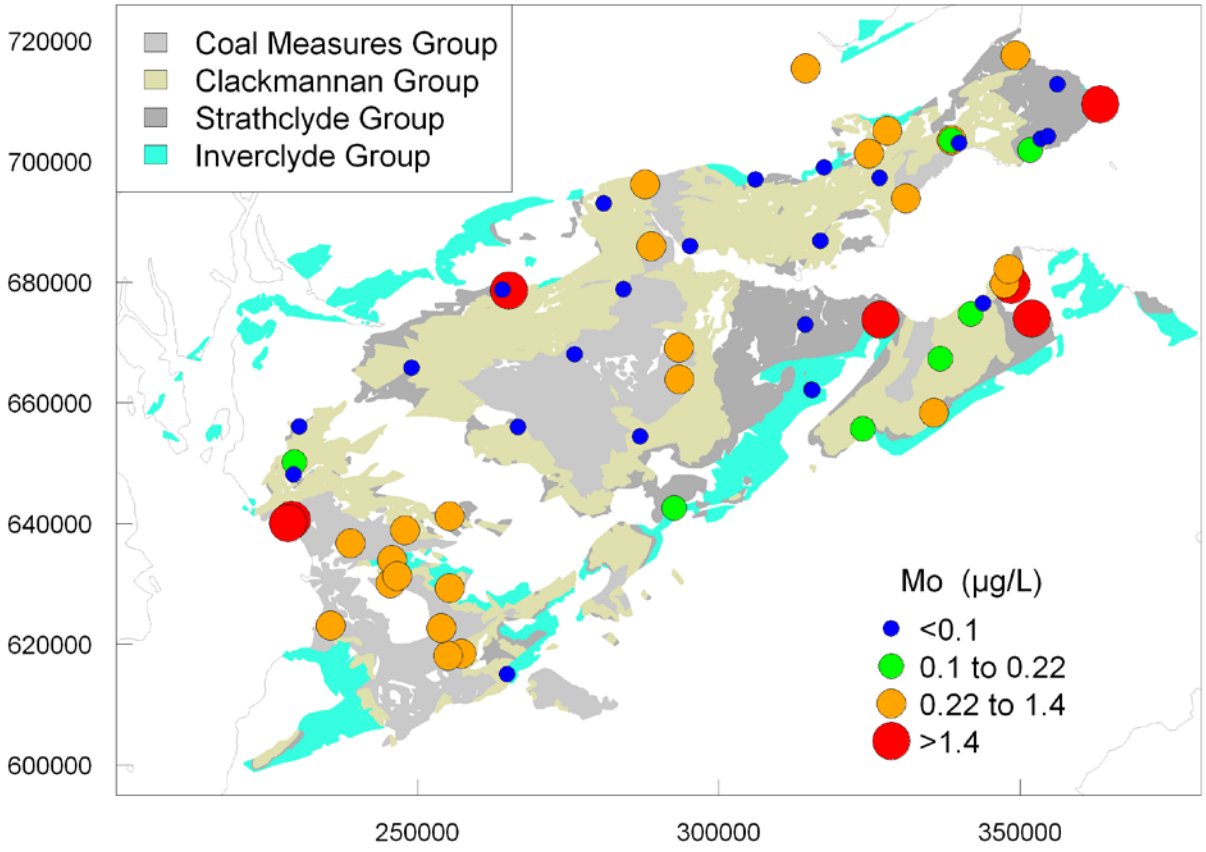


Figure 33 Box plot and map showing the distribution of molybdenum concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

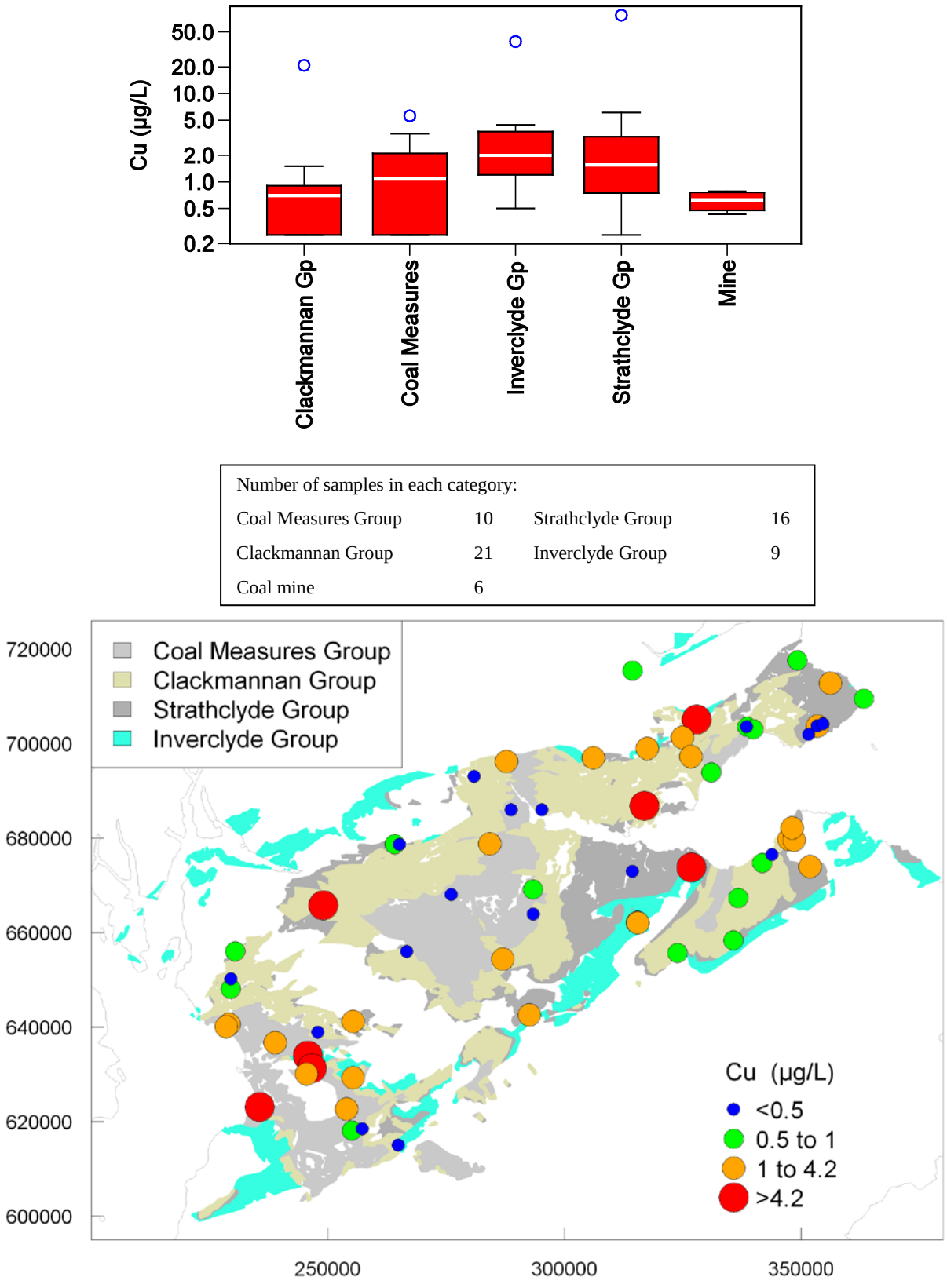
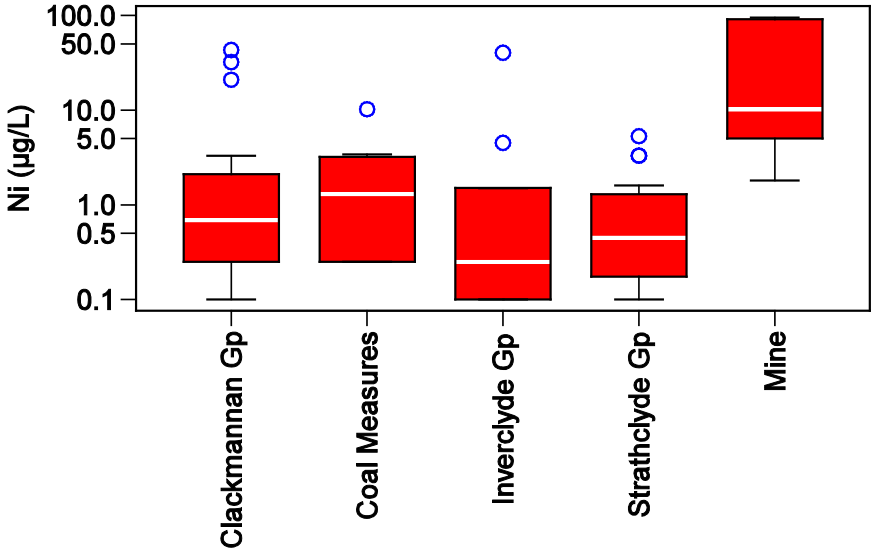


Figure 34 Box plot and map showing the distribution of copper concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

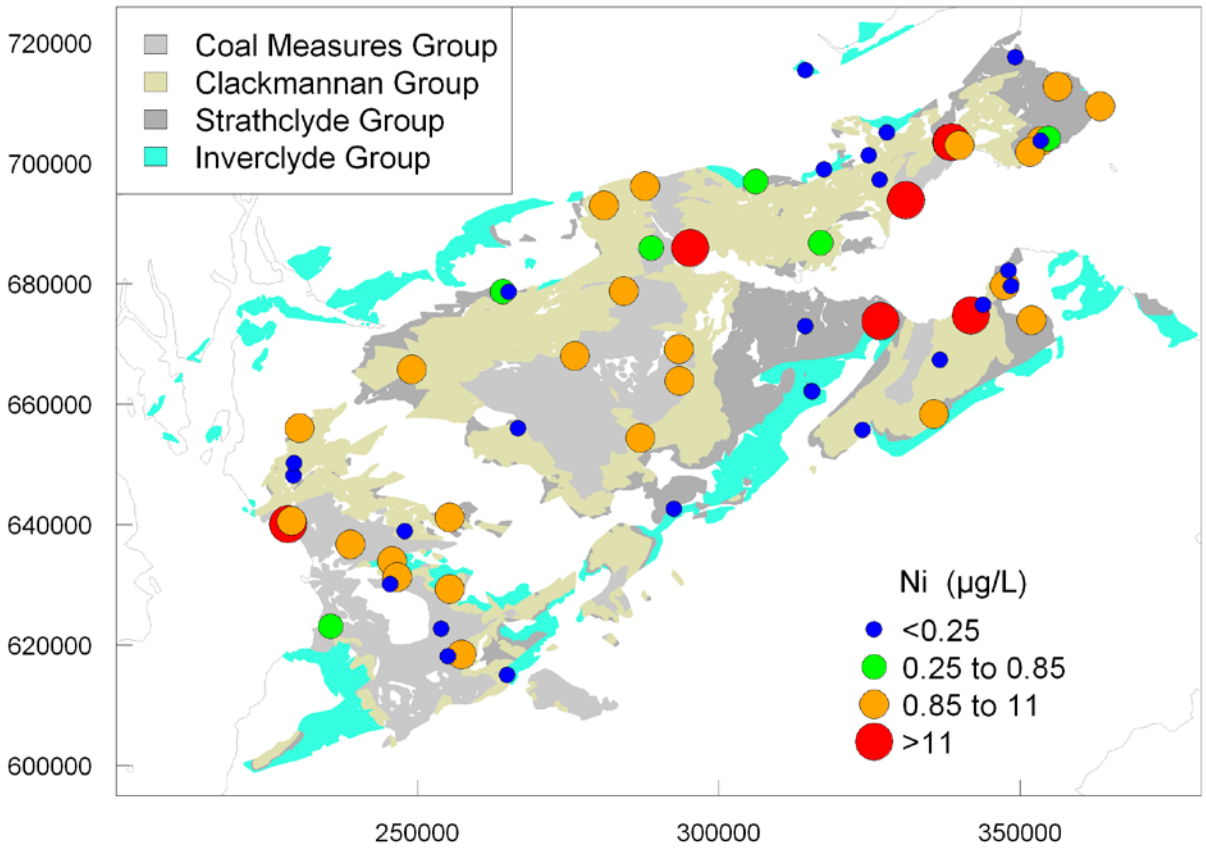
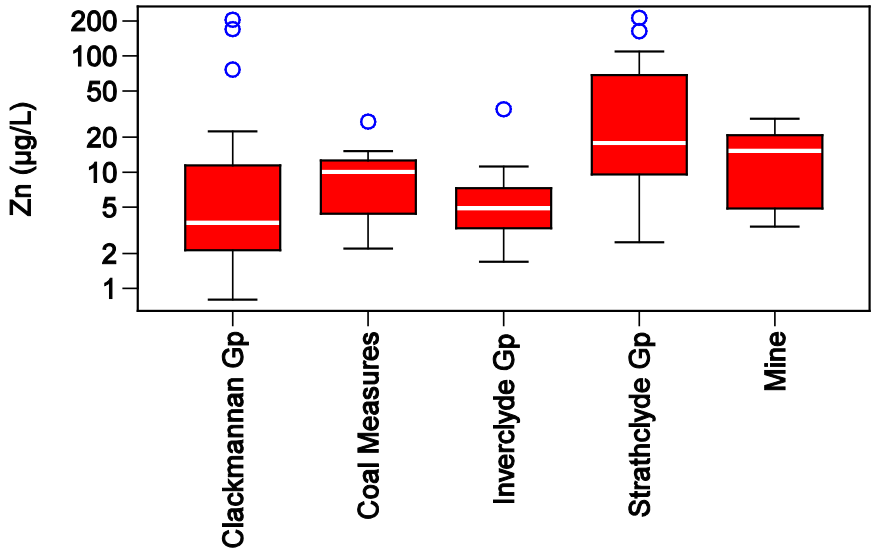


Figure 35 Box plot and map showing the distribution of nickel concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	6		

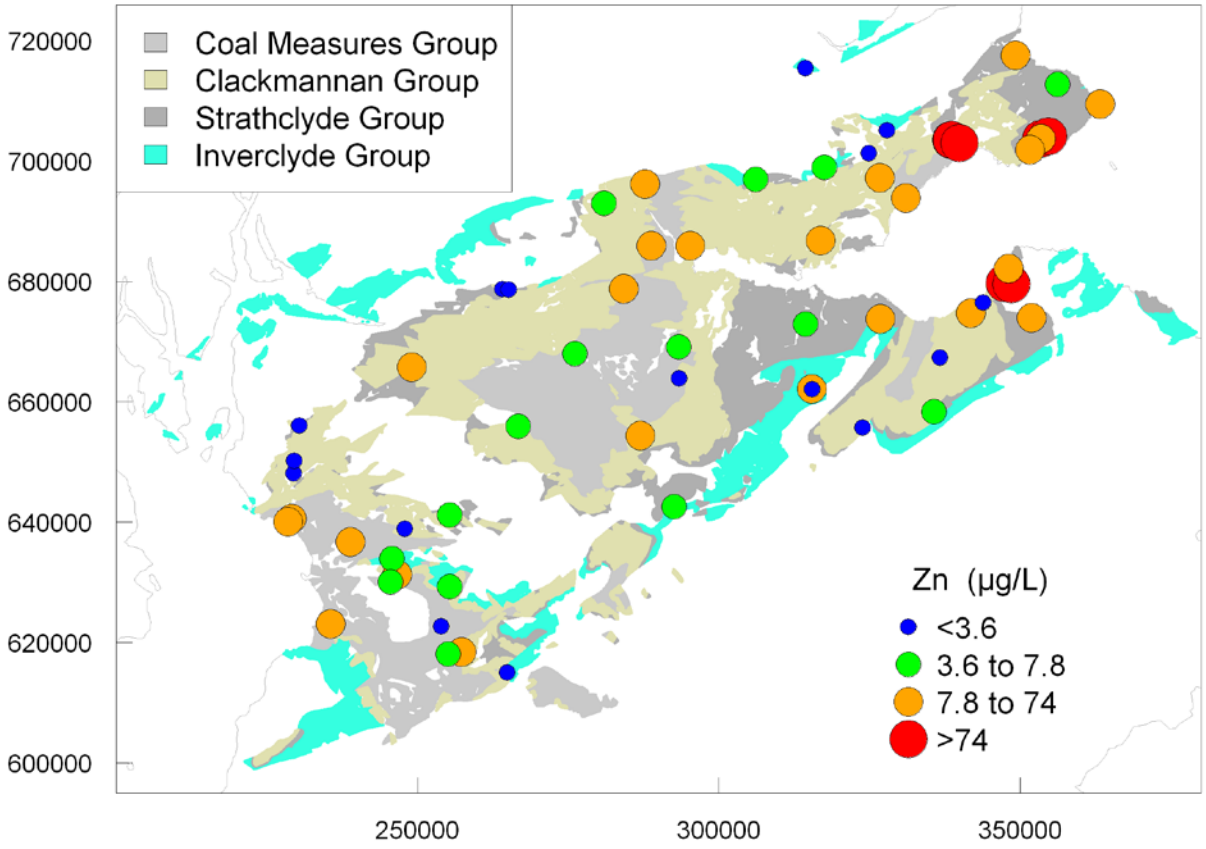
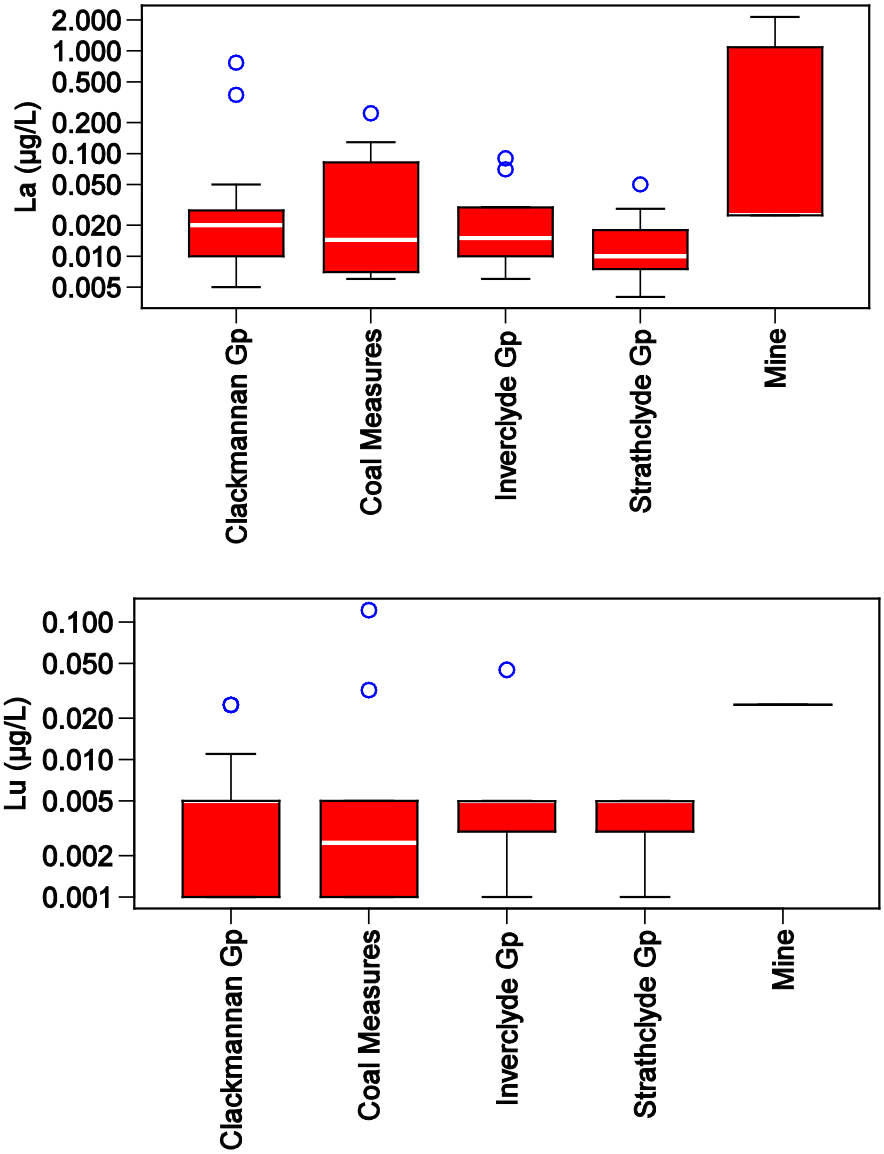


Figure 36 Box plot and map showing the distribution of zinc concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

4.4.12 Rare earth elements (REE)

Some very high REE concentrations are apparent in the groundwaters. ∑REE concentrations vary between 0.02 and 14.5 µg/L. Examples of representative REE concentrations in the different aquifer groups are shown in Figure 37. The highest ∑REE value observed occurs in the most acidic (pH 6.13), high-Fe sample, (Sample 57), from a 'Mine' water. The next highest ∑REE is much lower, at 4.6 µg/L. Groundwaters from the 'Mine' category in general have the highest REE concentrations. Some relatively high concentrations are also found in groundwaters from the Clackmannan and Coal Measures groups. Mobilisation of REE is most likely to have occurred as a result of reductive dissolution of Fe oxides (and release of adsorbed REE) under reducing conditions. REE release from clay minerals under acidic conditions generated by oxidation of pyrite is also possible, but the pH-buffered condition of most of the groundwaters would be unfavourable to maintaining the REE in soluble form.



Number of samples in each category:			
Coal Measures Group	10	Strathclyde Group	16
Clackmannan Group	21	Inverclyde Group	9
Coal mine	4		

Figure 37 Box plots showing the distribution of La and Lu concentrations in groundwaters from Carboniferous sedimentary aquifers across the Midland Valley

Compositions of REE normalised to the North Atlantic Shale Composite (NASC) (Figure 38) show that normalised concentrations are slightly heavy-REE enriched, with a slight negative Ce anomaly and a pronounced positive Eu anomaly. Complexation of heavy REE with dissolved carbonate species is a possible cause of the normalised heavy REE enrichment, especially given the high alkalinity of many of the groundwaters from the Midland Valley. The slight negative Ce anomaly suggests a decoupling of Ce from its neighbours (La, Pr). This can be a consequence of the variable oxidation state of Ce under differing environmental conditions. Unlike La and Pr, Ce can be present in a tetravalent (Ce(IV)) state and hence behave differently from its trivalent (REE(III)) neighbours. The large positive Eu anomaly is probably explained by dissolution of a Eu-rich mineral phase, such as plagioclase, in the sediments.

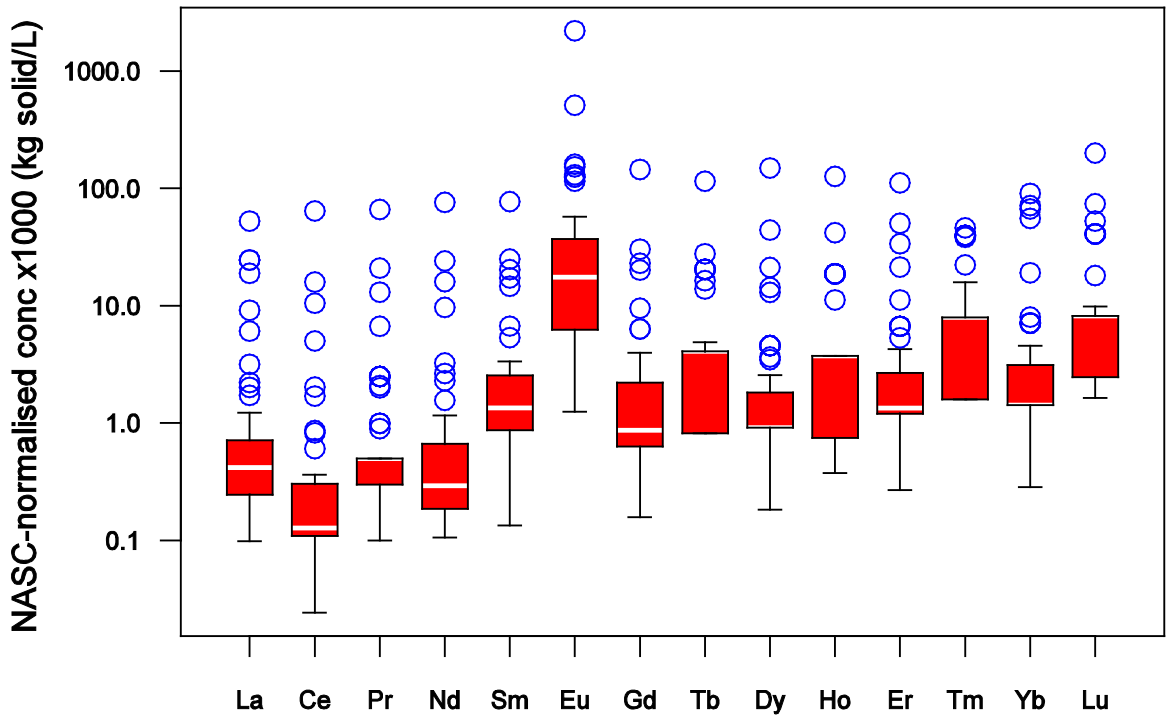


Figure 38 Box plot showing the distribution of the concentrations of REE normalised to the NASC 'average shale'

4.5 CUMULATIVE PROBABILITY PLOTS

Cumulative probability plots provide an alternative way of looking at the distribution of element concentrations. They are complementary to the box plots in Section 4.4. They are used here to provide a way of looking at a group of related elements in a single plot. The x-axis is the $\log_{10}$ transformed concentration while the y-axis gives the probability of a value exceeding a given concentration, plotted on a normal probability scale. The log transform was chosen as many elements, especially the trace elements, show a near log-normal distribution. The cumulative frequency (in percent) is 100 times the probability.

Although cumulative probability plots could be usefully sub-divided by aquifer group in the same way that the box plots, the limited number of samples in several of the aquifer groups means that the steps in the plotted distributions would be rather coarse, and any benefits would be likely outweighed by the increased crowding of the resulting plots. For the purposes of the cumulative probability plots, therefore, it is assumed that all 62 samples from the study area belong to a single population.

The plots make it easy to see the variation in the median concentrations between different elements (the points at which the probability is 0.5). The slopes of the lines give a measure of the variation (variance) of the subset of data and the straightness of the lines gives an indication of

the extent to which the distribution follows a log-normal distribution. A distinct change in slope may indicate that the overall distribution is made up of two or more sub-populations with differing statistical properties. A tailing at the high concentration end is common and may indicate a population of contaminated or mineralised sites. However, since there is no law of nature that dictates that a particular distribution should exist, it is not possible to infer the origin or genesis of particular sets of samples purely on the basis of their position within a population. This would require more information, including a model for what controls the concentration of a particular element within the sampled area. Similar reasoning applies to any attempt to distinguish 'natural' and 'contaminated' samples purely on the position within the overall distribution.

The cumulative probability plots were calculated on an element-by-element basis, with the elements grouped by their concentration ranges. Missing data were omitted. The NADA approach was chosen for calculating the probabilities, choosing the appropriate method for dealing with censored data according to the criteria outlined in Section 4.1. In most cases, the Kaplan-Meier method was used (see Section 4.1.1).

Cumulative probability plots are shown for the major ions and selected minor and trace elements (Figure 39, Figure 40 and Figure 41).

4.5.1 Major elements

The distribution of alkalinity (HCO_3) appears close to log-linear, although most other major ions (especially Na and Cl) have high tails, related to the presence of saline groundwaters. Na and Cl have similar distributions to each other, as do Ca, Mg and K. Distinct low tails are seen for both NO_3-N and SO_4, in response to reduction of both species (NO_3^- to N_2 or NH_4^+; SO_4^{2-} to HS^-) under reducing conditions in the aquifers.

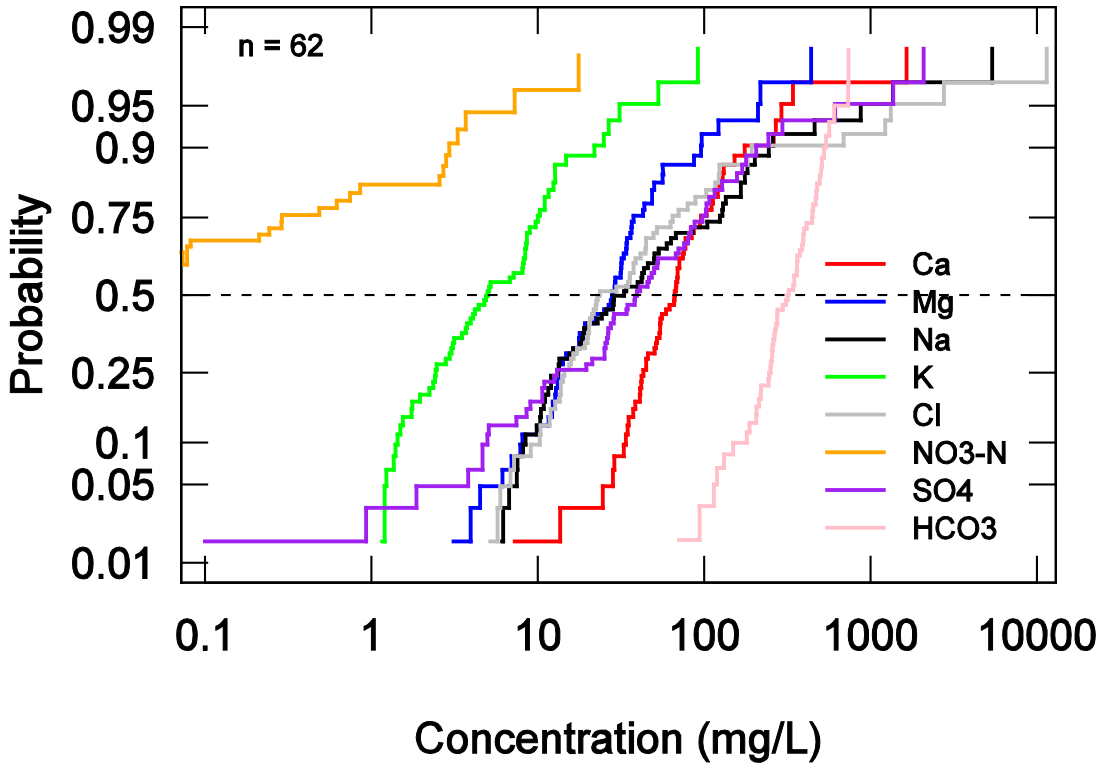


Figure 39 Cumulative probability plots for eight major elements.

4.5.2 Minor elements

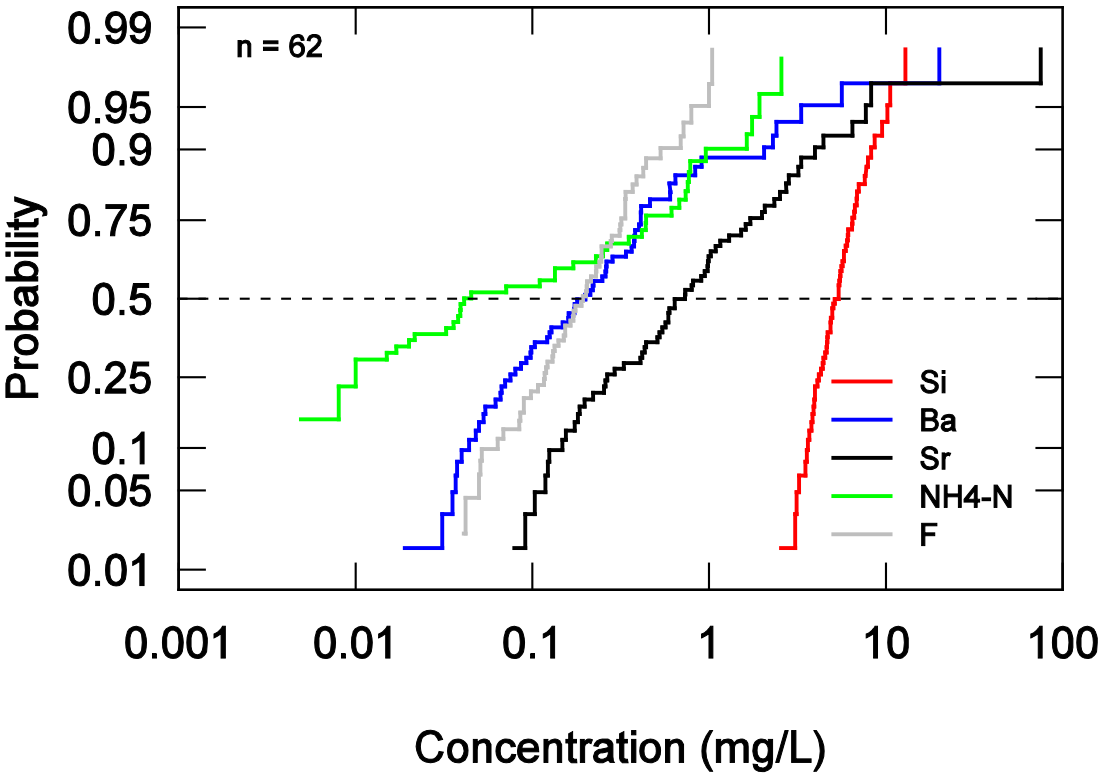
Silicon shows a steep near log-linear trend, indicating a relatively narrow range of concentrations (Figure 40). A good number of the waters sampled are saturated with respect to quartz, and precipitation of quartz is a likely control on the upper limit of dissolved Si concentrations. A high tail is seen especially for Sr and Br, again reflecting the presence of saline waters in the dataset. The distribution for Ba shows a slight curvature at the high end; almost all samples in the dataset are saturated with respect to barite and this will limit the upper concentrations of Ba. The distribution for F is close to log-linear and there is no evidence that concentrations are higher in the more mining-impacted waters. The distributions are not likely to be controlled by fluorite precipitation.

Curvature at the high end in the NH_4-N distribution (Figure 40) implies that the data belong to more than one population. The curvature at the high end results from the stabilisation of NH_4 under the most reducing conditions observed in the aquifers.

The shallow trend for NO_2 (Figure 40) appears to be related to the presence of NO_2 in some samples, as a result of nitrate reduction and the intermediate production of NO_2. Distributions of Fe and to a lesser extent Mn also show the wide range in compositions of these elements in the groundwaters.

4.5.3 Trace elements

Particularly high tails are seen for Cu, Pb and Zn (Figure 41), which all result from the high concentrations seen in the ‘Mine’ waters and other groundwaters that are impacted by oxidation of sulphide minerals.



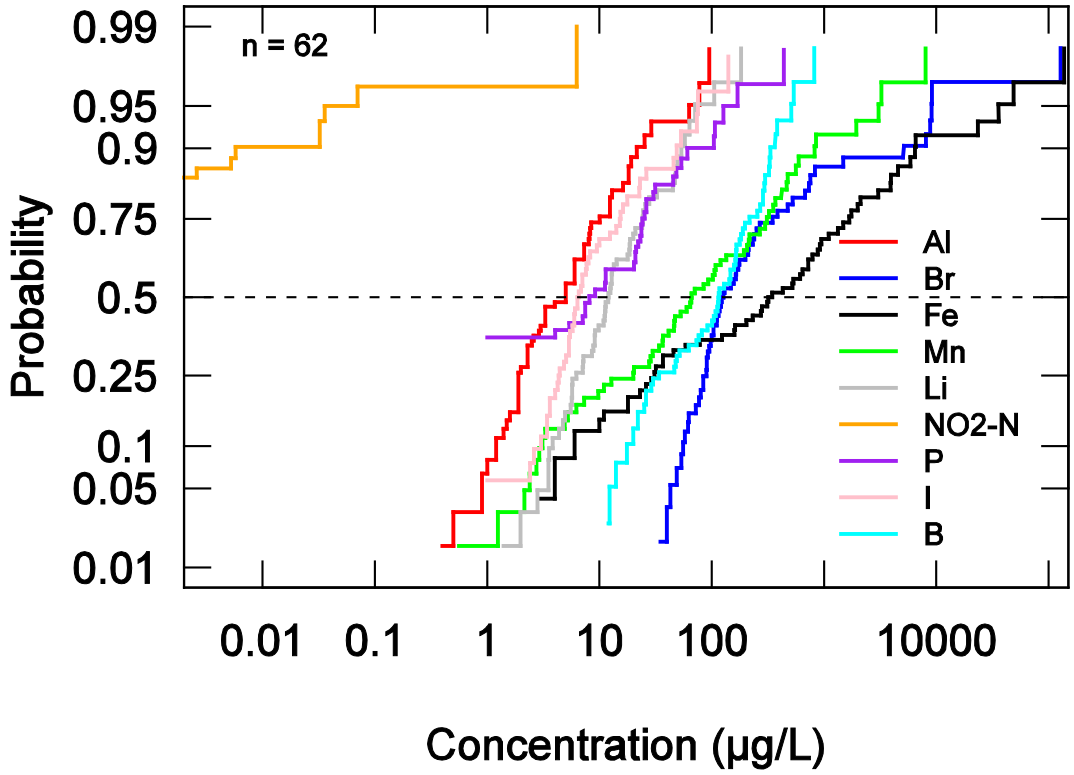


Figure 40 Cumulative probability plots for selected minor elements.

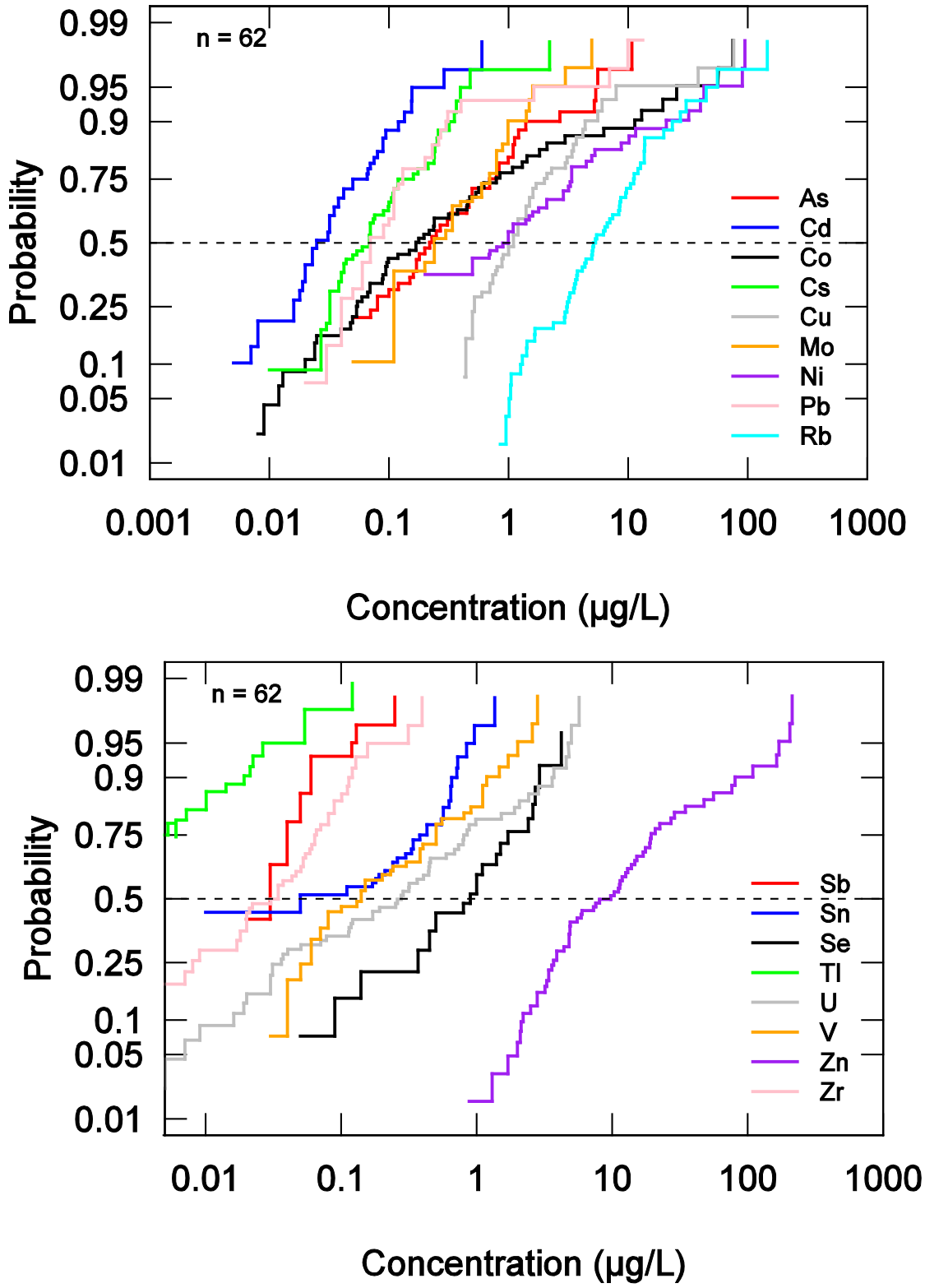


Figure 41 Cumulative probability plots for selected trace elements

4.6 ENVIRONMENTAL TRACERS

4.6.1 Stable isotopes

The topography of the Midland Valley is relatively subdued – the highest altitude sample is from 280 m OD (Sample 12) – and the groundwater samples show no simple correlation with altitude (Figure 42). The oxygen and hydrogen isotope composition of groundwaters is largely controlled by rainout effects as the predominantly southwesterly winds deliver moisture along the Midland Valley. There is a generally good correlation between the sample distance east from the west coast (the National Grid Reference Easting) and the amount of heavy isotope depletion (Figure 43). The two samples relatively enriched in $\delta^{18}O$ compared to their longitude (Samples 35 and 57), circled in blue in Figures 43 and 44) were from the eastern Midland Valley near the Firth of Forth, and illustrate the effect of minor enrichment sometimes encountered at coastal sites (Darling et al. 2003). The single sample with a very depleted isotopic composition (Sample 37), circled in red in Figures 43 and 44) is from the Stirling area. Two possible sources of this water are: (1) that it is of late-Pleistocene origin, although residence time analysis was not done for this sample so it is not possible to test this directly; or (2) that it derives from rainfall at higher altitudes in the Highlands to the northwest of Stirling, from where streams drain water into the River Teith, which then infiltrates into a shallow glaciofluvial aquifer. The interpretation of this sample is slightly complicated by the possible presence of sea water in the groundwater sampled, as indicated by the somewhat elevated Na, Cl and other elements, and by its proximity to an estuary. However, only a small proportion of seawater would be required to explain the observed chemistry, and would have little effect on the bulk isotope values.

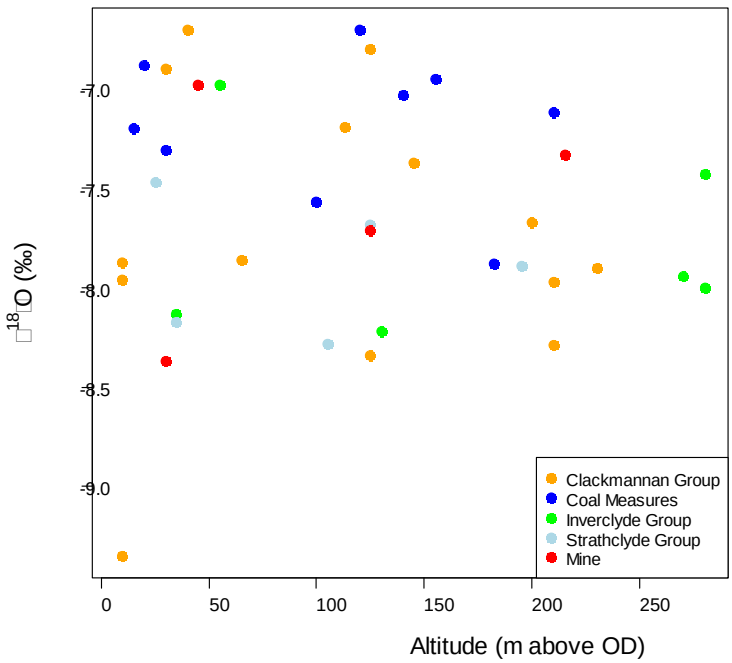


Figure 42 Plot of $\delta^{18}O$ versus altitude of sampling site

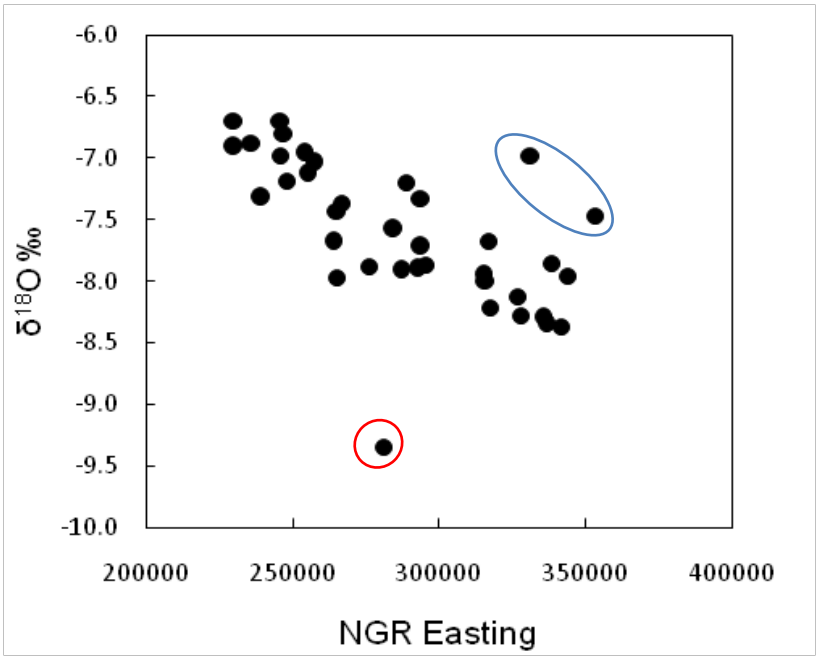


Figure 43 Plot of $\delta^{18}O$ in groundwater samples from Carboniferous sedimentary aquifers across the Midland Valley, versus NGR Easting, showing the isotopic depletion occurring owing to rainout from the predominantly southwesterly airstream. Circled samples are mentioned in the text.

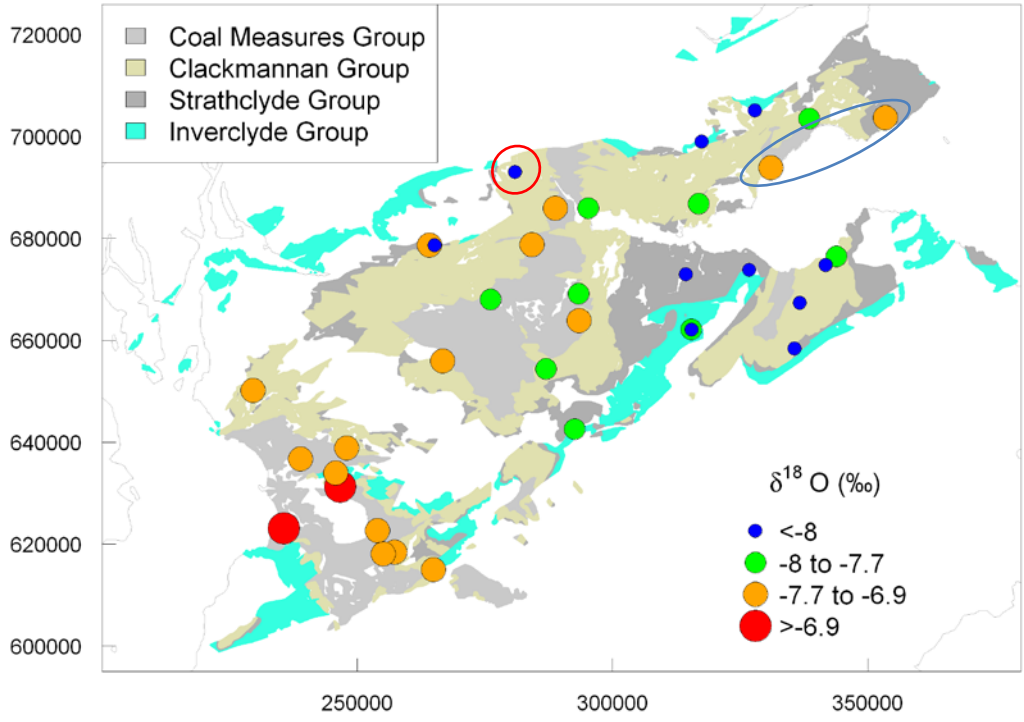


Figure 44 Map of $\delta^{18}O$ in groundwater samples from Carboniferous sedimentary aquifers across the Midland Valley. Circled samples are mentioned in the text.

Carbon stable isotopes indicate a basic progression as rock calcite (presumed to be marine in origin) dissolves into the groundwater, from dilute, poorly-buffered waters, with $\delta^{13}C$-DIC (dissolved inorganic carbon) values of < –20‰, to more mature waters with alkalinities of *c.* 500 mg/L as HCO_3 and $\delta^{13}C$ values of *c.* –10‰. However, there are some exceptions (Figure 45). The largest deviations occur to the left of the trend. Such deviations can be caused by DIC being derived by oxidation of organic carbon present in the groundwater system from sources such as coal and lignite. One of the samples analysed for methane (Section 4.6.3) was found to have a concentration of almost 6000 µg/L CH_4. At these relatively high concentrations,

oxidation of CH_4 will produce sufficient amounts of isotopically-depleted CO_2 (around -26‰ in $\delta^{13}C$) to affect the carbonate system and cause a deviation from the normal water–rock maturity trend. Methane was not measured on the sample with highest alkalinity and most depleted $\delta^{13}C$-DIC in Figure 45 (Sample 37) but this water is likely to by similarly affected, suggesting that the depleted O stable isotope values mentioned above, and the similarly depleted H stable isotope values also seen in the samples, are indicative of long residence rather than river infiltration.

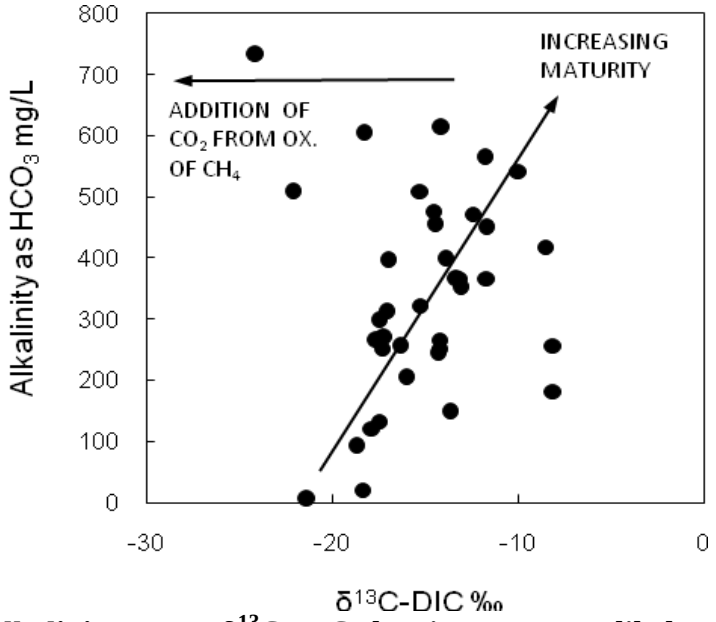


Figure 45 Plot of alkalinity versus $\delta^{13}C$-DIC showing processes likely to be operating

4.6.2 Recent age indicators

The dissolved atmospheric trace gases SF_6 (sulphur hexafluoride) and the CFCs (chlorofluorocarbons) were measured in selected samples to provide an indication of groundwater residence time. The interpretations of age made from such analyses are linked to the rise of these gases in the atmosphere, and therefore in rainfall, over the past half-century (Darling and Gooddy 2007). However, the CFCs can suffer breakdown under reducing groundwater conditions, and both SF_6 and the CFCs may be subject to contamination. Therefore, a certain amount of care is required in their interpretation. In addition, SF_6 is affected by the 'excess air' usually acquired by recently recharged groundwater as water tables undergo seasonal changes in level. To allow for this, the raw SF_6 concentration values have been multiplied by a correction factor of 0.75[1].

Figure 46 shows groundwater CFC-11 and CFC-12 (two key CFC species) concentrations respectively, plotted versus excess-air-corrected SF_6 concentrations. Also shown are the theoretical concentrations anticipated from equilibrium between the atmosphere and groundwater recharge over the past few decades, assuming a recharge temperature of 10°C – the so called 'piston flow' (PF) curve, and the binary mixing (BM) line between modern and old (pre-CFC in the atmosphere) groundwater.

[1] Based on the assumption of a 3 ccSTP/L excess air component

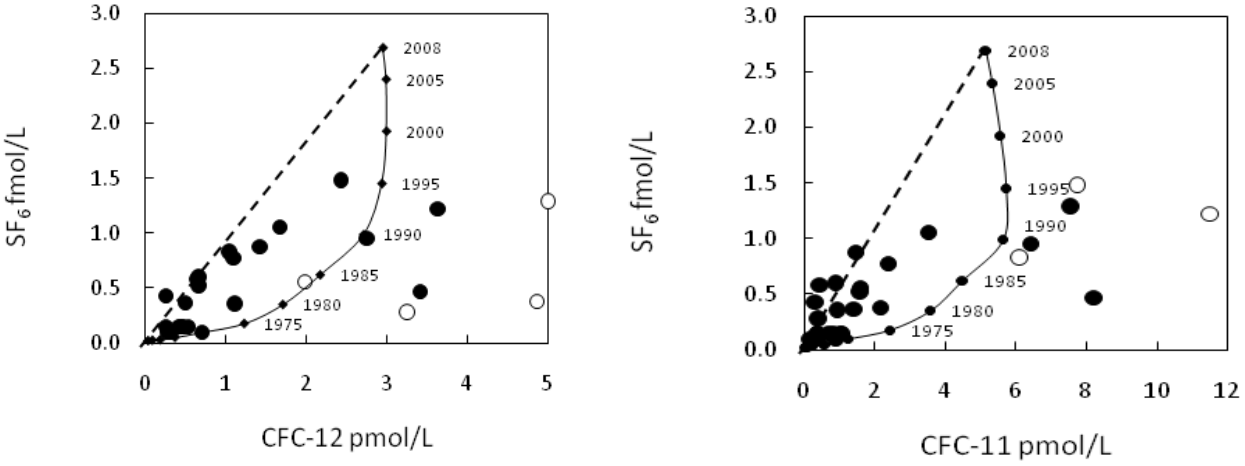


Figure 46 Plots of CFC-12 and CFC-11 versus SF_6 concentrations. Also shown are the theoretical piston flow curve (solid line, small circles; labelled by year) and the binary mixing line (dashed), assuming a recharge temperature of 10°C. Where there is a lack of relative agreement, open (white) circles indicate where CFC-12 or CFC-11 is the higher of the pair (see text).

Where both the CFC-12 and CFC-11 plots (Figure 46) show individual samples in approximately the same position relative to the binary mixing-piston flow (BM-PF) envelope it is usually assumed they can be directly interpreted in age or mixing terms. Where there are significant differences, further consideration is necessary. Where CFC-11 exceeds CFC-12, the difference can be attributed to contamination: CFC-11 is more prone to contamination. In the four cases where CFC-12 exceeds CFC-11 and is beyond the PF–BM envelope (shown by open (white) circles in the CFC-12 plot in Figure 46), there has probably been contamination of both CFCs, but CFC-11 has subsequently undergone microbial reduction in low oxygen groundwaters (in all of these four cases dissolved oxygen concentration is less than 0.2 mg/L). Where there is disagreement between the CFCs, the SF_6 value should be used alone to infer residence time, and the hydrogeology used to interpret whether a binary mixing or piston flow mechanism is more likely.

In the Midland Valley, most samples give similar results for CFC-12 and CFC-11 versus SF_6, allowing interpretation (Figure 46). This mainly suggests that the groundwaters are either dominated by piston flow (PF) with ages usually >35 years (though one sample is only 15 years old), or by binary mixing (BM), where older water usually forms more than two-thirds of the sample. Many of the results are intermediate, falling between the two lines, and are assumed to represent a form of 'exponential' flow, i.e. the product of a distribution of ages around a mean value.

In summary, the data show that the majority of the groundwaters in the Carboniferous aquifers of the Midland Valley are likely to contain a high proportion of relatively old water, recharged more than 35 years ago, and a significant proportion recharged more than 60 years ago. There is evidence of mixing of various groundwaters; however, the stable isotope data did not indicate the widespread presence of palaeowaters (Pleistocene waters >10,000 years old).

4.6.3 Other dissolved gases

Concentrations of carbon dioxide (CO_2) and methane (CH_4) were measured on selected groundwaters. Carbon dioxide concentrations are governed by carbonate equilibria, with higher concentrations expected in lower pH waters. The highest CO_2 concentration in the dataset was found in the water with the lowest pH (Sample 57) (Figure 47a). At this value (pH 6.13), more than half the DIC would be in the form of CO_2.

In approximately half the samples measured, CH_4 was present at 10 µg/L or less (Figure 47b), typical of values found in major aquifers like the Chalk and Sherwood Sandstone of England (Gooddy and Darling 2005). The remainder of the samples range up to *c.* 10 mg/L. Waters with CH_4 concentrations higher than 1.5 mg/L can in principle give rise to explosive atmospheres in confined situations such as buildings and excavations (Hooker and Bannon 1993; Gooddy and Darling 2005). Three samples exceeded this value (Figure 47b). In England, high concentrations of CH_4 have also been found in groundwaters from Carboniferous sedimentary rocks (Gooddy and Darling 2005).

In the two samples with the highest CH_4 concentrations, higher alkanes were also measured. The sample with the highest concentration (Sample 55) had a C_1/C_2 molar ratio of *c.* 120, which tends to suggest the methane is the product of methanogenesis taking place in a landfill or within slurry. The sample with the second highest concentration (Sample 38), from the >1000 m deep borehole, in the Coal Measures Group, had a C_1/C_2 ratio of *c.* 6, associated with coal sources of methane.

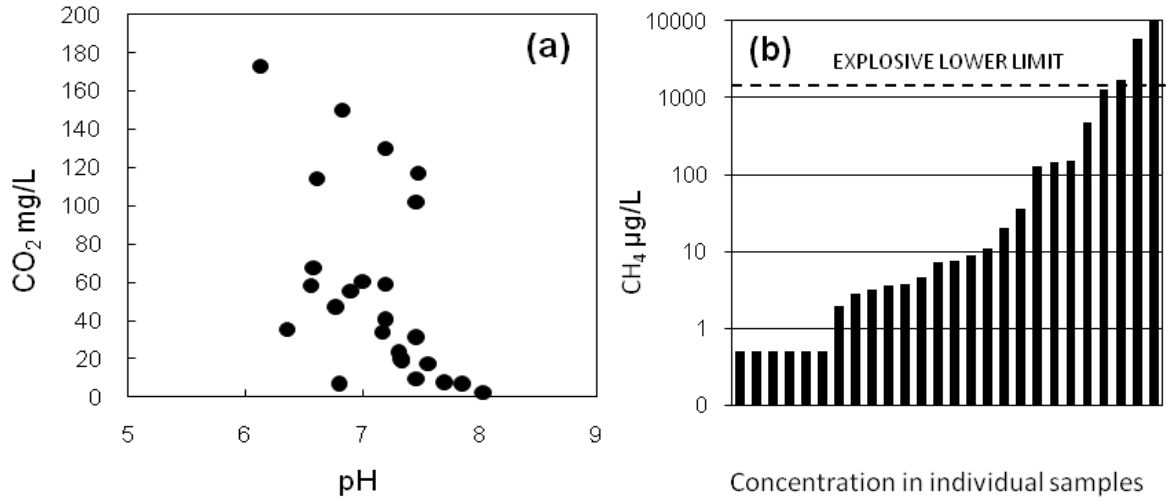


Figure 47 (a) plot of CO_2 concentration versus pH in groundwaters from Carboniferous sedimentary rocks of the Midland Valley, showing the tendency for an increase in CO_2 as pH falls; (b) range of CH_4 concentrations found, with explosive hazard limit shown.

5 Discussion

5.1 BASELINE GROUNDWATER CHEMISTRY

One of the reasons for undertaking this survey was to determine the baseline groundwater chemistry conditions for different hydrogeological units in the Carboniferous sedimentary aquifers of the Midland Valley. Baseline chemistry can incorporate a range of chemical concentrations in groundwater in any one aquifer, influenced by natural processes, such as oxidation state and residence time. However, many of the samples have been influenced by human activity, particularly related to mining and to agricultural practices. In defining baseline conditions we have excluded the six samples which specifically targeted coal mine discharges. However, we have kept samples that may have been influenced by mining activities. Whether or not mining-impacted chemical reactions are considered anthropogenic rather than natural is a matter of debate, but the inclusion of mine-impacted groundwaters here is meant to emphasise that mining impacts on groundwater chemistry are an exaggeration of a set of geochemical processes that can, and do, occur under natural conditions.

To try and define the natural baseline chemistry of groundwater unaffected by human activity, two main approaches have been taken, as for previous Baseline Scotland reports (Ó Dochartaigh et al. 2006, MacDonald et al. 2008, Smedley et al. 2009). The first is statistical; a secondary approach involves selecting individual samples from each aquifer group which are judged to be representative of baseline conditions.

The main approach to defining baseline groundwater chemistry is statistical, and assesses the natural variation in baseline chemistry that can occur. Under this approach, the data between the 10th and 90th percentiles are examined for each element or ion. Using only data between the 10th and 90th percentiles allows the influence of outliers to be minimised. New groundwater chemistry data from the same aquifers would be expected to plot within this range 80% of the time. Data outwith this range can still occur naturally, but are less common, and therefore may merit some further investigation.

The baseline statistics are presented first for the groundwaters from all groups of Carboniferous sedimentary aquifers in the Midland Valley except the ‘Mine’ category (Table 3). The overall major ion distribution for the five hydrogeological units distinguished is illustrated in a Piper diagram (Figure 48). Summary statistics are also presented for each of the five units (Appendix 2), and the overall chemistry of groundwater from each unit is summarised briefly.

The large range in major ion compositions illustrated by the Piper diagram (Figure 48) indicates the large number of processes, many of them natural, which have affected the groundwaters. These processes include carbonate dissolution reactions, redox reactions (including pyrite oxidation), ion exchange, mixing with saline water and variations in residence time.

In other areas of Scotland, the two parameters which have been modified substantially by anthropogenic (mainly agricultural) activity, and for which concentrations cannot usually be regarded as representing ‘baseline’ conditions, are nitrate and phosphorus. In the Midland Valley, however, any anthropogenic influence has been itself significantly modified by the redox conditions in the aquifer. More detail is given in Section 5.4.

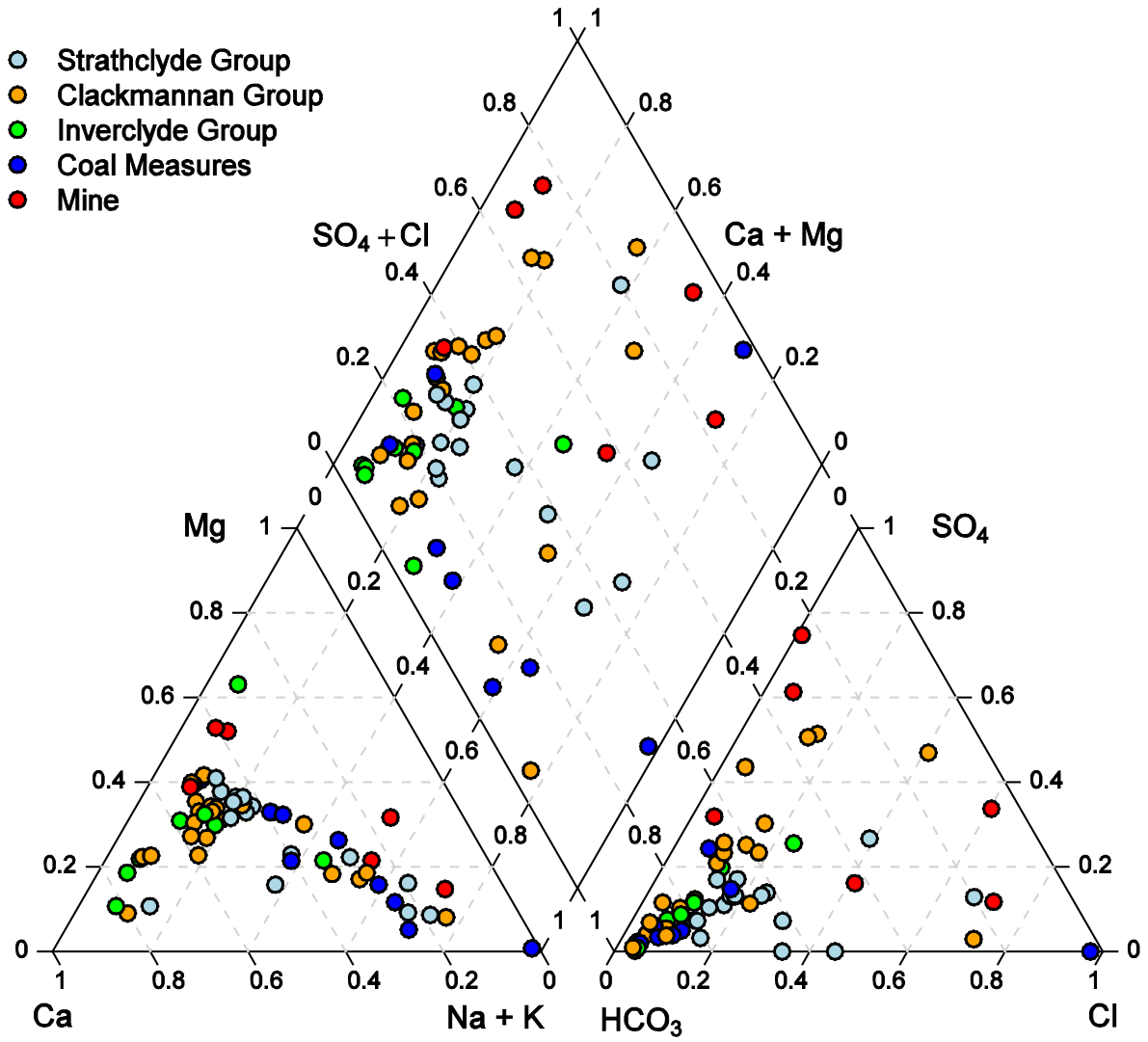


Figure 48 Piper diagram showing the compositions of groundwater from Carboniferous sedimentary aquifers across the Midland Valley

Table 3 Summary statistics for chemical elements in sampled groundwaters from all sedimentary Carboniferous aquifers across the Midland Valley except 'Mine' waters. Summary statistics for individual aquifer categories are presented in Appendix 2.

Elem	Units	No.	No. cens	min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	55	0	7.1	8	9	10.3	11.3	13.7	14.6	17.9	KM
pH		55	0	6.15	6.4	6.6	7.2	7.46	7.85	8.12	8.99	KM
Eh	mV	43	0	31	136	178	226	308	359	380	414	KM
DO	mg/L	45	1	<0.11	0.2	0.8	1.8	3.05	7.62	9.3	10.8	KM
SEC	µS/cm	56	0	137	321	415	688	976	1380	2400	31800	KM
d^2H	‰	34	0	<63.9	42.9	45.4	48.8	53.2	54.5	56.6	<41	KM
$d^{18}O$	‰	34	0	<9.35	6.88	7.12	7.67	7.97	8.28	8.34	<6.7	KM
$d^{13}C$	‰	34	0	<24.2	10	13.4	15.3	17.5	18.7	22.1	3.1	KM
Ca	mg/L	56	0	3.4	28.8	41	56	76.6	123	269	1640	KM
Mg	mg/L	56	0	1.08	6.98	12.8	21.5	33.6	48.2	86.9	210	KM
Na	mg/L	56	0	5.59	7.6	11.6	28.3	67.4	182	259	5360	KM
K	mg/L	56	0	0.64	1.36	2.23	4.08	8.58	12.4	21.9	92.2	KM
Cl	mg/L	56	0	5.14	7.22	13.6	22.4	49.8	123	692	11500	KM
SO_4	mg/L	56	1	<0.1	4.65	10.6	28.7	70.4	115	179	244	KM
HCO_3	mg/L	54	0	7	132	221	276	398	508	606	736	KM
NO_3.N	mg/L	45	26	<0.05				0.487	2.95	3.71	17.7	KM
NO_2.N	mg/L	45	36	<0.02							6.3	ROS
NH_4.N	mg/L	44	11	<0.01	0.002	0.005	0.036	0.264	0.736	0.957	1.75	KM
P	µg/L	56	26	<20			7	24	60	125	432	KM
DOC	mg/L	32	0	0.45	0.56	0.91	1.2	1.6	2.26	47.1	70.8	KM
F	mg/L	55	0	0.033	0.052	0.108	0.189	0.32	0.531	0.793	1.04	KM
Br	µg/L	56	1	<100	54	81	117	235	846	9060	127000	KM
I	µg/L	46	3	<2	2.6	4.2	6	12.3	44.8	72.5	139	KM
Si	mg/L	56	0	1.95	3.5	3.93	5.06	6.18	8.23	10.2	12.9	KM
Al	µg/L	56	0	0.2	1	1.6	3	6	18	28.7	94	KM
As	µg/L	56	22	<0.5		0.06	0.17	0.5	1.4	5.4	10.8	KM
B	µg/L	56	3	<20	14	26	109	184	329	371	536	KM
Ba	mg/L	56	0	0.019	0.048	0.08	0.199	0.396	2.05	3.32	20.1	KM
Be	µg/L	56	36	<0.05	0.0001	0.0004	0.002	0.008	0.020	0.063	0.289	ROS
Cd	µg/L	56	21	<0.05	0.001	0.008	0.023	0.042	0.094	0.155	0.29	KM
Ce	µg/L	56	6	<0.05	0.004	0.009	0.01	0.02	0.071	0.413	1.31	KM
Co	µg/L	56	2	<0.05	0.013	0.05	0.12	0.48	2.12	13.1	25.8	KM
Cr	µg/L	56	37	<0.5	0.0554	0.0972	0.173	0.306	0.75	0.9	2.2	ROS
Cs	µg/L	56	6	<0.05	0.01	0.03	0.05	0.105	0.26	0.396	2.21	KM
Cu	µg/L	56	11	<0.5	0.3	0.5	1	2	4.4	20.9	77	KM
Dy	µg/L	56	22	<0.05	0.002	0.003	0.006	0.009	0.019	0.078	0.241	KM
Er	µg/L	56	26	<0.05		0.002	0.004	0.006	0.016	0.08	0.188	KM
Eu	µg/L	56	4	<0.05	0.007	0.01	0.03	0.059	0.2	0.257	3.54	KM
Fe	µg/L	56	2	<10	4	23	234	951	3940	6520	35600	KM
Ga	µg/L	56	36	<0.05	0.0036	0.0060	0.011	0.024	0.032	0.040	0.176	ROS
Gd	µg/L	56	14	<0.05	0.001	0.002	0.005	0.01	0.04	0.127	0.192	KM
Ge	µg/L	24	19	<0.05	0.00144	0.00377	0.0121	0.039	0.107	0.229	0.39	ROS
Hf	µg/L	56	42	<0.05	0.004	0.005	0.007	0.01	0.01	0.012	0.03	ROS
Hg	µg/L	24	12	<0.1				0.6	1	1.2	1.4	KM
Ho	µg/L	56	33	<0.05	9.92E-5	0.0003	0.001	0.002	0.004	0.018	0.056	ROS
La	µg/L	56	6	<0.05	0.006	0.01	0.014	0.028	0.082	0.247	0.768	KM

Elem	Units	No.	No. cens	min	10%	25%	50%	75%	90%	95%	max	method[1]
Li	µg/L	56	0	1.24	3.5	5.6	10.9	18.4	32.1	57.6	182	KM
Lu	µg/L	56	41	<0.05	7.42E-5	0.00023	0.00080	0.003	0.006	0.016	0.122	ROS
Mn	µg/L	56	0	0.45	2.74	9.74	47.7	209	465	597	1950	KM
Mo	µg/L	56	16	<0.2		0.1	0.2	0.6	1	1.6	5	KM
Nd	µg/L	56	10	<0.05	0.005	0.007	0.01	0.02	0.087	0.365	0.911	KM
Ni	µg/L	56	24	<0.5	0.14	0.14	0.5	2.1	5.3	32.1	43.1	KM
Pb	µg/L	56	14	<0.1	0.02	0.03	0.06	0.12	0.3	1.63	13.3	KM
Pr	µg/L	56	24	<0.05	0.001	0.002	0.003	0.004	0.01	0.067	0.21	KM
Rb	µg/L	56	0	0.47	1.05	2.94	4.97	8.61	13.5	23.4	145	KM
Re	µg/L	24	16	<0.01	0.0002	0.0006	0.0022	0.01	0.02	0.046	0.09	ROS
Rh	µg/L	24	14	<0.01	0.0004	0.0011	0.0034	0.01	0.017	0.046	0.1	ROS
Sb	µg/L	56	25	<0.05	0.01	0.01	0.02	0.03	0.05	0.12	0.25	KM
Se	µg/L	21	5	<0.5	0.09	0.37	0.9	1.7	2.7	2.9	4.2	KM
Sm	µg/L	56	22	<0.05	0.002	0.004	0.006	0.013	0.04	0.129	0.186	KM
Sn	µg/L	56	26	<0.08			0.04	0.38	0.66	0.85	1.37	KM
Sr	mg/L	56	0	0.039	0.122	0.219	0.587	1.16	3.96	7.68	74.9	KM
Th	µg/L	56	35	<0.05	0.0003	0.0008	0.0032	0.01	0.024	0.057	0.979	ROS
Ti	µg/L	56	25	<10	0.01	0.02	0.05	0.14	0.57	0.67	13	KM
Tl	µg/L	56	42	<0.05	0.0001	0.0003	0.0009	0.004	0.017	0.023	0.119	ROS
TON	mg/L	24	16	<1	0.0103	0.0182	0.101	0.372	2.55	4.06	7.7	ROS
U	µg/L	56	3	<0.05	0.009	0.03	0.169	0.727	3.55	4.74	5.71	KM
V	µg/L	56	9	<0.2	0.03	0.05	0.13	0.4	1.18	2.27	2.8	KM
Y	µg/L	56	12	<0.05	0.02	0.03	0.05	0.09	0.27	0.8	1.09	KM
Yb	µg/L	56	22	<0.05	0.002	0.003	0.005	0.01	0.016	0.195	0.318	KM
Zn	µg/L	56	0	0.8	2.1	3.3	7.3	18.9	80.4	170	212	KM
Zr	µg/L	56	16	<0.05	0.002	0.007	0.03	0.06	0.113	0.155	0.392	KM

[1]Statistical method (for more details see Section 4.1.1). Where >80% of samples were non-detects, ranges only are quoted

No. Cens: number of censored observations

KM: Kaplan-Meier, used when <50% of the samples in the dataset are censored

ROS: Regression on Order Statistics, used when >50% of the samples in the dataset are censored

TON: Total Organic Nitrogen

As a secondary approach to identifying baseline groundwater chemistry, 11 groundwater samples from across the Midland Valley have been selected as representative both of the likely natural groundwater chemistry and of the general observed range in chemical variation. All were sampled from sources where there is little or no indication of direct contamination, including likely impact from mining. These can be used as reference groundwaters for management purposes. The chemistry of each sample broadly falls within the 10^{th} to 90^{th} percentile ranges for each aquifer, as presented in Appendix 2. Unlike in other study areas within the Baseline Scotland project, NO_3 concentrations were not used as an indicator of contamination, because of the evidence for widespread nitrate reduction linked to the reducing nature of groundwaters in the Carboniferous aquifers of the Midland Valley.

At least two samples were chosen from each aquifer: two from the Strathclyde Group; three from the Inverclyde Group; two from the Coal Measures Group; and four from the Clackmannan Group. The samples represent a range of land uses: semi-natural, agricultural (improved grassland pasture, arable and mixed cultivated), urban/industrial, and recreational. The location of the baseline samples related to the aquifer distribution is shown in Figure 49, and the samples are highlighted in Appendix 1.

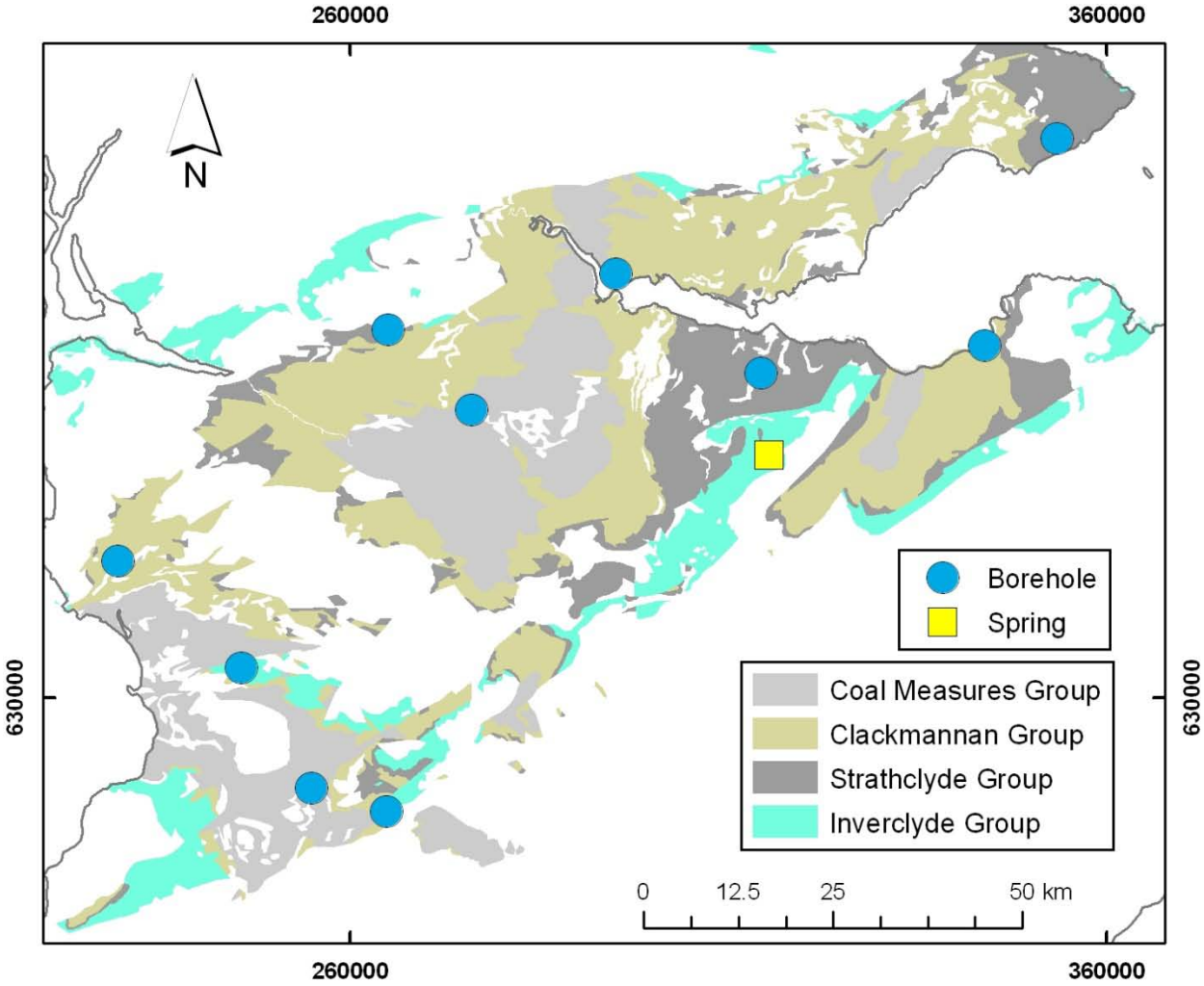


Figure 49 Location of the eleven representative baseline groundwater samples from Carboniferous aquifers across the Midland Valley

5.1.1 Baseline groundwater chemistry by aquifer

A summary of the overall chemistry of groundwater from each of the four non-mine hydrogeological units of the sedimentary Carboniferous aquifers in the Midland Valley is presented here. The chemistry of the minewater samples is described in Section 5.3.

Summary statistics for chemical parameters in groundwater from each of the hydrogeological units are presented in Appendix 2.

COAL MEASURES GROUP

Groundwaters from the Coal Measures Group are generally of bicarbonate type, with cations either dominated by Na or with no dominant cation. There was one Na-Cl type groundwater, from the only very deep (*ca* 1000 m) borehole sampled.

Average alkalinity values are the highest of all the hydrogeological units sampled, including the 'Mine' waters (median HCO_3 456 mg/L; 10^{th} -90^{th} percentile range 251–510 mg/L). The range in SEC values is large (10^{th}–90^{th} percentile range 274 to 1220 µS/cm) and the median value (889 µS/cm) is the highest for all the groups except 'Mine' waters. The waters are generally anoxic (the 95^{th} percentile of dissolved oxygen was 1.7 mg/L; median 0.95 mg/L) and slightly acidic to near-neutral, with the lowest average pH of all the aquifer groups except 'Mine' waters (pH 6.33–7.34; median 6.96).

The groundwaters typically have moderate concentrations of Ca (10^{th} to 90^{th} percentile range, 3.4–76.6 mg/L; median 50.2 mg/L), Mg (10^{th}-90^{th} percentile range 1.08–43.3 mg/L; median 19 mg/L), Cl (12–45 mg/L; median 19 mg/L) and SO_4 (10^{th}-90^{th} percentile range,4.98–52.5 mg/L; median 21.2 mg/L). Concentrations of Na were high relative to other geological groups (10.4–134 mg/L; median 59.6 mg/L). In most cases the calcite saturation index showed the groundwaters were close to saturation.

Iron and Mn concentrations show a large range (10^{th} to 90^{th} percentile range for Fe 4–5890 µg/L; for Mn 1.24–475 µg/L) but are usually high, with the highest average of any group except the 'Mine' waters (median Fe 1110 µg/L; median Mn 107 µg/L). Concentrations are linked to the redox conditions of the groundwater (Homoncik et al. 2010).

CLACKMANNAN GROUP

Groundwaters from the Clackmannan Group are generally either of Ca-Mg-HCO_3 type Na or have no dominant anion; a few show a cationic dominance of Na. One sample (Sample 46) is of Na-Cl type; it has been subject to considerable cation exchange.

The groundwaters typically have high HCO_3 concentrations (10^{th}–90^{th} percentile range 94–508 mg/L; median 265 mg/L), with a near-neutral pH (median 7.2). They generally have low dissolved oxygen (10^{th} to 90^{th} percentile, 0.2–5.05 mg/L; median 1.2 mg/L). SEC values showed a wide range with a moderate average (10^{th}–90^{th} percentile range 310–1130 µS/cm; median 596 µS/cm).

The waters generally had moderate to high concentrations of Ca (10^{th}–90^{th} percentile range 28.8–123 mg/L; median 54.5), Mg (7.86–36.4 mg/L; median 17.5 mg/L); Na (8.2–134 mg/L; median 15.5 mg/L) and Cl (7.22–64.7 mg/L; median 20.7 mg/L). Concentrations of SO_4 were the highest of all the hydrogeological units except 'Mine' waters (10^{th}–90^{th} percentile range 9–107 mg/L; median 48.5 mg/L).

Most of the samples were significantly undersaturated with respect to calcite.

Iron and Mn concentrations were moderate to high (Fe 10^{th}–90^{th} percentile range 26–3940 µg/L; median 322 µg/L; Mn 7.27–465 µg/L; median 103 µg/L). Variability is due to the redox conditions in the aquifer.

INVERCLYDE GROUP

Most of the groundwaters from the Inverclyde Group were of Ca-HCO_3 type. They typically have moderate HCO_3 concentrations (10^{th}–90^{th} percentile range 188–313 mg/L; median 256 mg/L) with a near-neutral pH (median 7.3 mg/L). Dissolved oxygen concentrations are generally low but most of the waters are not anoxic (10^{th} to 90^{th} percentile range 0.16–7.62 mg/L; median 2.3 mg/L). SEC values are typically moderate (10^{th} to 90^{th} percentile range 177–695 µS/cm; median 510 µS/cm).

The groundwaters typically had relatively low concentrations of Na (10^{th} to 90^{th} percentile range 5.59–20.1 mg/L; median 8.5 mg/L), Cl (10^{th}–90^{th} percentile range 5.74–20.5 mg/L; median 12.8 mg/L) and SO_4 (10^{th}–90^{th} percentile range 0.93–28.7 mg/L; median 13 mg/L), with moderate concentrations of Ca (38.4–70.6 mg/L; median 66 mg/L) and Mg (6.16–27.2 mg/L; median 19 mg/L).

In most cases the calcite saturation index showed the groundwaters were close to saturation.

Iron and Mn concentrations were typically relatively low (10^{th}–90^{th} percentile range for Fe 2–205 µg/L and median 18 µg/L; and for Mn 0.45–71.3 µg/L and median 6.18 µg/L), reflecting the generally oxic nature of the groundwaters from this group.

STRATHCLYDE GROUP

Most of the groundwaters sampled from the Strathclyde Group were of Ca-Mg-HCO_3. Some samples are more dominated by Na with no anionic dominance.

The groundwaters typically have moderate HCO_3 concentrations (10^{th}–90^{th} percentile range 150–452 mg/L; median 278 mg/L) with near-neutral pH (median 7.1 mg/L). Dissolved oxygen concentrations are usually low but most of the waters are not anoxic (10^{th}–90^{th} percentile range 0.8–3.76 mg/L; median 2.5 mg/L). SEC values are generally moderate to high (10^{th}–90^{th} percentile range 355–1380 µS/cm; median 738 µS/cm).

The groundwaters typically had moderate concentrations of Ca (10^{th}–90^{th} percentile range 32.8–120 mg/L; median 56 mg/L) and SO_4 (0.15–170 mg/L; median 34.2 mg/L) and moderate concentrations of Na (10^{th}–90^{th} percentile range 10.5–202 mg/L; median 43.7 mg/L), Cl (17.3–183 mg/L; median 44.9 mg/L) and Mg (8.08–55.5 mg/L; median 28.9 mg/L).

In about half of the samples the calcite saturation index showed the groundwaters were close to saturation or saturated with respect to calcite; the other half were undersaturated.

Iron concentrations are relatively low on average but show a wide range (10^{th}–90^{th} percentile range 4–1690 µg/L; median 79 µg/L). Mn concentrations are typically moderate (10^{th}–90^{th} percentile range 2.39–209 µg/L; median 37.1 µg/L).

5.2 EXCEEDANCES ABOVE DRINKING WATER STANDARDS

The Baseline Scotland survey is not intended to provide an assessment of drinking water quality in the study area. Few (less than 30%) of the samples collected are from sources which are used for drinking water and where they are, the samples collected were usually not collected from drinking-water taps. The analyses cannot therefore be taken as strictly representative of the quality of water from groundwater sources used for drinking in the area. Nonetheless, some of the sample sources are private supplies which are at least in part used for drinking water. The samples were collected from as close to the wellhead as possible. Water supplied from these sources to drinking water supply points may have undergone some subsequent form of treatment or storage (e.g. aeration, chlorination, UV filtration or settling). The Baseline Scotland data can therefore provide an overall indication of drinking water quality, but are not a substitute for specific water testing at the point of use.

With these caveats in mind, the data provide a general sense of the inorganic constituents of the groundwaters which may provide problems from a drinking water supply perspective. Scottish drinking water quality limits are governed by the Water Supply (Water Quality) (Scotland) Regulations (2001) and the Private Water Supplies (Scotland) Regulations (2006), which give equivalent limits for most inorganic parameters (the exceptions are Ag and Zn which have limits only in the latter regulations). In the samples analysed, the most common exceedances of these limits were for Fe, Mn, Na and NH_4. Some 58% of the waters sampled had Fe concentrations greater than the limit for Fe in public supply drinking water of 200 µg/L; 13% had concentrations of Mn greater than the limit of 50 µg/L; and 11% had concentrations greater than the limit for Na of 200 mg/L. The regulations stipulate NH_4 as an indicator parameter with a concentration limit of 0.39 mg/L as N; 28% of analysed samples were in excess of this value.

Nitrite and nitrate were present in excess of the respective drinking water limits in one sample for each parameter (different samples for each). The high NO_3 sample was from a source used for a private drinking water supply.

Some 20% of the analysed waters had pH values less than the national minimum required value of 6.5, though none exceeded the upper pH limit of 9.5.

In addition, six samples (10%) had Ni concentrations exceeding 20 µg/L. These were mostly from the Clackmannan Group and 'Mine' waters; none is thought to be a drinking water source.

Arsenic was each present in one sample from the dataset at a concentration above the drinking water limit of 10 µg/L. The same sample had a Pb concentration of 13.3 µg/L, which is above the 2013 limit for Pb (10 µg/L), although it does not exceed the current limit (25 µg/L).

Note that no organic compounds (e.g. microbial counts, pesticides, or solvents) were measured in this study and no inference is therefore made on the occurrence of these compounds in the groundwaters of the region.

5.3 MINING

Mining activity has had a major impact on groundwater quality in the region. This is the case with some groundwaters from the Coal Measures and Clackmannan groups, as well as the samples identified as 'Mine' waters.

The effects of mining activities, as well as of water-rock interactions that take place naturally in sulphide-mineralised environments, can give rise to high concentrations of Fe and SO_4 through pyrite oxidation, and this appears to be the case in the Midland Valley. No widespread corresponding increases in trace metals such as Ni, Cu, Zn and Pb are seen. This is similar to examples from the South Wales coalfield, where Fe is the main contaminant, with concentrations of other metals typically no higher than background concentrations in local rivers (Wiseman et al 2003). Manganese concentrations are elevated in many of the 'Mine' waters in the Midland Valley as a result of reducing conditions. Increased mineral content, in particular alkalinity, and the near neutral pH of the 'Mine' waters is attributed to the dissolution of carbonate minerals that buffers the acidity produced by pyrite oxidation.

The six samples of groundwater known to be sourced from abandoned coal mines are of a wide range of chemical types. Of the cations, three show a dominance by Ca/Mg and three by Na/(K). The anions are variable: two are dominated by SO_4, two by Cl, one by HCO_3 and one shows no dominant anion.

Alkalinity of the 'Mine' waters is the highest of all the aquifer groups (10^{th}–90^{th} percentile range 346–525 mg/L; median 417 mg/L) and the samples are typically slightly acidic, with the lowest median pH (6.61) of all the groups. The waters are usually anoxic. SEC values are typically high (10^{th}–90^{th} percentile range 740–5040 µS/cm; median 1430 µS/cm).

The 'Mine' waters show wide ranges but typically high concentrations of Ca (10^{th}–90^{th} percentile range 66.4–262 mg/L; median 131 mg/L), Mg (36.2–17 mg/L; median 95.5 mg/L),

and SO_4 (103–1380 mg/L; median 296 mg/L), and similarly large ranges but moderate to high concentrations of Na (10^{th}–90^{th} percentile range 16.3–873 mg/L; median 63 mg/L) and Cl (13.8–1330 mg/L; median 44.4 mg/L). Calcite saturation indices are variable, with one sample being strongly undersaturated and most of the rest close to saturation.

Iron and Mn concentrations are often very high (Fe 10^{th}–90^{th} percentile range 135– 48,600 μg/L and median 2010 μg/L; Mn 196–3280 μg/L and median 852 μg/L).

Five of the other samples – two from the Clackmannan Group and three from the Coal Measures Group – were collected from boreholes or shafts known or strongly suspected to intercept abandoned mine workings. Although none of these sources was specifically abstracting mine waters, it is likely that at least some of the groundwater pumped from them derives from the mine workings. These five samples tend to be more mineralised than samples which are thought unlikely to be affected by mining, although generally not as mineralised as the 'Mine' waters. This is particularly the case for concentrations of HCO_3, K, SO_4, Fe and Mn, and for SEC. Average Ca concentrations in these five samples are as high as those in the 'Mine' waters. Average concentrations of Cl, Mg and Na in these samples are similar to those in samples thought unlikely to be impacted by mining.

5.4 NITRATE AND PHOSPHORUS

Concentrations of NO_3 are in most cases low. This is in keeping with the low oxygen, NO_3-reducing nature of many of the groundwaters, and because of the often confined nature of the Carboniferous aquifers, regardless of land use. The groundwaters more commonly have high concentrations of NH_4, in line with their often strongly reducing nature. In no cases could NH_4 occurrence be attributed confidently to anthropogenic origins. Concentrations of P are more variable, but only in a few cases are high concentrations considered to be potentially of anthropogenic origin. High concentrations of P are in many cases likely to be from natural reactions with minerals and carbonaceous material in the aquifers.

5.5 GROUNDWATER FLOW IN THE MIDLAND VALLEY

The hydrochemistry data and information on groundwater residence times help to give an insight into groundwater flow in the Carboniferous sedimentary aquifers of the Midland Valley.

The majority of the groundwaters are likely to contain a high proportion of relatively old water, recharged more than 35 years ago, and a significant proportion (>60%) appear to have been recharged more than 60 years ago. There is no evidence of the presence of palaeowaters (older than 10,000 years) in the Midland Valley; however, there is some evidence for mixing between younger waters and deeper more mineralised water in some locations.

6 Conclusions

The groundwater chemistry of Carboniferous sedimentary aquifers in the Midland Valley has been investigated using new chemistry analyses, generated during the Baseline Scotland project, combined with existing analyses from earlier projects. The chemistry of groundwater from five hydrogeological units (or aquifer groups) has been examined: four chronostratigraphic groups, which in decreasing order of age are the Inverclyde, Strathclyde, Clackmannan and Coal Measures groups; and a fifth group incorporating waters sampled from mine discharges.

A total of 62 groundwater analyses were interpreted for the purposes of this study. Of these, 36 analyses were from samples collected for the Baseline Scotland project between September and December 2008. These were augmented with data for a further 25 samples collected during separate BGS projects since 2001. The sites were chosen largely to be representative of groundwater in the area, and sources that were very poorly constructed were avoided. A small number of samples were deliberately targeted from mines, either from adits, shafts or boreholes.

An estimate of the baseline groundwater chemistry conditions in the four chronostratigraphic hydrogeological units is presented, based on a statistical summary of the chemical data, which represents values between the 10^{th} and 90^{th} percentiles of the full dataset range.

This statistical approach to estimating baseline characteristics was complemented by selecting 11 analyses for groundwaters collected from sources where there is little or no indication of direct contamination, including likely impact from mining. The chemistry of these samples represents typical groundwater conditions in the four non-mine hydrogeological groups in the sedimentary Carboniferous aquifers of the Midland Valley.

A summary of the conclusions arising from this study follows.

Groundwater flow

1. Many of the groundwater samples from the studied aquifers are from deep boreholes, where groundwater is often present under confined conditions and within multilayered aquifers. Groundwater flow is dominated by flow within fractures. Analysis of dissolved gases and stable isotopes indicate that groundwaters contain a high proportion of relatively old water, recharged more than 35 years ago, and a significant proportion of water recharged more than 60 years ago. However, there is little evidence of the existence of palaeowater (older than 10,000 years).

2. Many of the groundwaters show evidence of having been impacted by ion-exchange reactions (Na for Ca exchange), which suggests that young shallow groundwater has mixed with older, more mineralised water.

Baseline chemistry

3. The groundwaters show a very wide range of solute concentrations, with a 10^{th}–90^{th} percentile range of TDS values of 274 to 1620 mg/L, and a median of 555 mg/L. The lowest TDS value was from groundwater from a spring, which also had the lowest alkalinity. The highest TDS was in reducing groundwater from a deep borehole (>1000 m) in the Coal Measures Group. There are some distinct differences in groundwater chemistry between the aquifer groups. The most mineralised groundwaters (excluding mine discharges) are from the Coal Measures Group, which also have the lowest dissolved oxygen concentrations, At least some of the groundwaters identified as being from the Coal Measures Group are likely to have been impacted in some way by coal mining, The least mineralised groundwaters were from the Inverclyde and Strathclyde groups.

4. Groundwater pH is usually near-neutral, with a 10^{th}–90^{th} percentile range of 6.40 to 7.84. There is little apparent difference in pH between the different aquifer groups. The pH data indicate that the acid buffering capacity of the aquifers is high (even for mine discharges), most probably controlled by dissolution of carbonate minerals. Alkalinity is variable but often high, with a 10^{th}–90^{th} percentile range for the dataset of 132 to 510 mg/L. The main species contributing to groundwater alkalinity is HCO_3. The highest median alkalinity values are in the Coal Measures Group, although some high concentrations also occur in the Clackmannan Group.

5. Many of the collected groundwaters are reducing (anoxic), with 37% of determined dissolved oxygen values less than or equal to 1 mg/L and 60% of determined Eh values less than 250 mV. Groundwaters from the Clackmannan Group and Coal Measures groups are the most reducing (excluding the mine discharges). Field sampling showed evidence (by smell) that some of the groundwater sources from the Clackmannan and Coal Measures groups contained dissolved sulphide, indicating the presence of strongly reducing conditions in some parts of these aquifers. Detectable dissolved methane was measured in a number of the samples. Samples from the Strathclyde and Inverclyde groups show the highest dissolved oxygen concentrations. High concentrations of dissolved organic carbon (DOC) (up to 70.8 mg/L) in a few samples are also indicative of the reducing – often strongly reducing – nature of some of the groundwaters.

6. Groundwater types encompass a large range from Ca-HCO_3, through Ca-Mg-HCO_3, through SO_4-rich types, Na-HCO_3, and (rarely) Na-Cl. The groundwaters have variable calcite saturation indices but in many cases are close to saturation, indicating both the presence of and reaction with carbonate minerals in the aquifers.

7. There is a wide range in concentrations of the major anions. Concentrations of Cl are typically high, but 10^{th} percentile 7.2 mg/L and 90^{th} percentile 123 mg/L. The highest value (11,500 mg/L) is from a very deep (>1000m) borehole. Concentrations of SO_4 span some five orders of magnitude, with a 10th–90th percentile range of 4.7–179 mg/L. The overwhelmingly dominant processes controlling this large range are likely to be oxidation of sulphide minerals, particularly in mining-impacted waters; and sulphate reduction in the most reducing conditions. Low concentrations (<5 mg/L SO_4) are usually associated with low NO_3-N concentrations and often high NH_4<N; all samples recorded in the field as having a smell of H_2S had SO_4 concentrations <5 mg/L.

8. There is large spatial variability in concentrations of the major cations. The highest concentrations of Ca and Mg are in mine waters and some Coal Measures Group groundwater, probably due to reaction of carbonate minerals, and clays, which could have been enhanced by the generation of acid during the oxidation of iron sulphide. Concentrations of Na are also often high, particularly in groundwaters from the Coal Measures and Clackmannan groups and mine waters. Concentrations of K are also correspondingly high. The high concentrations of dissolved cations are likely to reflect the effects of extreme water-rock interaction, in some cases (particularly deep boreholes) involving long residence times in the aquifers concerned. Sodium is probably largely sourced from dissolution of silicate minerals and ion-exchange reactions, the latter induced by young shallow groundwater mixing with older saline water..

9. Concentrations of Fe and Mn show large ranges, consistent with the large variations in redox status in the aquifers. The highest Fe and Mn concentrations are in groundwater from the Coal Measures Group and Clackmannan Group. Both elements are found at highest concentrations in groundwaters with low dissolved oxygen concentrations, in agreement with the recent findings of Homoncik *et al.* (2010).

Nitrate and phosphorus

10. The distribution and large variations in NO_3-N concentrations also show the strong control that redox conditions have on groundwater chemistry, indicating that denitrification – which occurs under reducing conditions – has been important in many of the groundwaters. Nitrite is detectable in a few low-NO_3 groundwaters and, as an intermediate reaction product, is an additional indication of denitrification. Concentrations of NH_4-N are high in a number of samples, in several exceeding 1 mg/L, and are consistent with degradation of natural organic matter in the aquifers. The distribution of N species supports evidence from other redox-sensitive parameters that groundwaters from the Coal Measures Group and mine discharges are the most strongly reducing.

11. The highest P concentrations are in the Coal Measures and Clackmannan groups, with sources likely to include dissolution of phosphate minerals, desorption from iron oxides under reducing conditions and degradation of organic matter. Agricultural pollution may be contributory in some cases, but some of the outlier P concentrations occur in the more reducing (and mine-impacted) groundwaters, which would be consistent with a natural (mineral, organic matter) origin.

Dissolved gases

12. Dissolved carbon dioxide (CO_2) was measured on selected groundwaters and the results indicate that pCO_2 is often high, controlling carbonate equilibrium. Dissolved methane (CH_4) was present at 10 µg/L or less in approximately half the samples measured. Such values are typical of those found in major aquifers such as Cretaceous Chalk and the Permo-Triassic Sherwood Sandstone Group. The remainder of the samples range up to *ca.* 10 mg/L. Waters with dissolved CH_4 concentrations higher than 1.5 mg/L can in principle give rise to explosive atmospheres in confined situations such as buildings and excavations.

Mining

13. Mining activity has had a major impact on groundwater quality in the region. This is particularly the case for the samples collected directly from discharges (pumped or gravity flows) from abandoned coal mines. The mine-discharges are strongly mineralised, with high SEC values and particularly high concentrations of HCO_3, Ca, SO_4, Fe and Mn. The waters are generally low in dissolved oxygen and show the evidence of pyrite oxidation within the mines. The pH values are generally well-buffered and alkalinity is high, indicating significant reaction with carbonate material in the aquifers. Similar groundwater chemistry is also found in some other groundwaters, particularly from the Coal Measures and Clackmannan Groups, which were collected from boreholes or shafts that do not abstract mine waters directly, but that are suspected to intercept abandoned mine workings. Mine waters may therefore impact areas away from obvious sources of mine discharge.

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Appendix 1 Description of sampling sites

ID	Lab Sample ID	Project	Aquifer	Source type	Depth (m)	Land use
1	S02-00228	Orig NO_3 [1]	Strathclyde Group	Borehole	unknown	Recreational
2	S02-00229	Orig NO_3	Strathclyde Group	Borehole	30-100 m	Arable
3	S02-00230	Orig NO_3	Strathclyde Group	Borehole	unknown	Arable
4	S02-00266	Orig NO_3	Strathclyde Group	Borehole	30-100 m	Recreational
5	S02-00267	Orig NO_3	Strathclyde Group	Borehole	>100 m	Arable
6	S02-00268	Orig NO_3	Strathclyde Group	Borehole	30-100 m	Arable
7	S02-00269	Orig NO_3	Strathclyde Group	Borehole	>100 m	Improved grassland
8	S02-00270	Orig NO_3	Clackmannan Group	Borehole	30-100 m	Arable
9	S02-00271	Orig NO_3	Clackmannan Group	Borehole	30-100 m	Arable
10	S02-00278	Orig NO_3	Strathclyde Group	Borehole	>100 m	Recreational
11	S02-00296	Orig NO_3	Inverclyde Group	Borehole	30-100 m	Mixed cultivated
12	**S04-01099**	**Springs**	**Inverclyde Group**	**Spring**	**0**	**Semi natural**
13	S04-01100	Springs [2]	Inverclyde Group	Spring	0	Semi natural
14	S05-00246	SGMN 3	Strathclyde Group	Borehole	30<100 m	Industrial/urban
15	S05-00250	SGMN	Inverclyde Group	Borehole	30<100 m	Semi natural
16	S05-00251	SGMN	Clackmannan Group	Spring	0	Arable
17	S05-00253	SGMN	Clackmannan Group	Well	<5 m	Improved grassland
18	S05-00256	SGMN	Strathclyde Group	Spring (possibly artesian borehole)	unknown	Identified DPP [5]
19	S05-00262	SGMN	Coal Measures	Borehole	30-100 m	Arable
20	S05-00263	SGMN	Inverclyde Group	Spring	0	Semi natural
21	S05-00285	SGMN	Clackmannan Group	Borehole	>100 m	Industrial/urban
22	S05-00286	SGMN	Clackmannan Group	Borehole	>100 m	Identified DPP
23	S05-00297	SGMN	Strathclyde Group	Borehole	30-100 m	Industrial/urban
24	S05-00614	Baseline	Clackmannan Group	Borehole	30-100 m	Improved grassland
25	S06-00382	Irvine [4]	Mine	Borehole	>100 m	Industrial/urban
26	S06-00383	Irvine	Mine	Borehole	>100 m	Industrial/urban
27	**S08-01082**	**Baseline**	**Clackmannan Group**	**Borehole**	**30-100 m**	**Recreational**
28	S08-01083	Baseline	Strathclyde Group	Borehole	30-100 m	Identified DPP
29	S08-01084	Baseline	Clackmannan Group	Borehole	unknown	Arable
30	S08-01085	Baseline	Clackmannan Group	Adit/Mine	unknown	Improved grassland
31	S08-01086	Baseline	Inverclyde Group	Borehole	unknown	Industrial/urban
32	S08-01087	Baseline	Strathclyde Group	Borehole	30-100 m	Mixed cultivated
33	S08-01088	Baseline	Inverclyde Group	Borehole	30-100 m	Mixed cultivated
34	**S08-01089**	**Baseline**	**Clackmannan Group**	**Borehole**	**>100 m**	**Mixed cultivated**
35	**S08-01090**	**Baseline**	**Strathclyde Group**	**Borehole**	**30-100 m**	**Arable**
36	S08-01091	Baseline	Clackmannan Group	Borehole	30-100 m	Arable
37	S08-01092	Baseline	Clackmannan Group	Borehole	30-100 m	Industrial/urban
38	S08-01093	Baseline	Coal Measures	Borehole	>100 m	Arable
39	S08-01096	Baseline	Coal Measures	Borehole	30-100 m	Identified DPP
40	**S08-01097**	**Baseline**	**Coal Measures**	**Borehole**	**>100 m**	**Industrial/urban**

ID	Lab Sample ID	Project	Aquifer	Source type	Depth (m)	Land use
41	S08-01098	Baseline	Clackmannan Group	Spring	0	Industrial/urban
42	S08-01099	Baseline	Strathclyde Group	Borehole	>100 m	Identified DPP
43	S08-01100	Baseline	Coal Measures	Borehole	>100 m	Identified DPP
44	**S08-01101**	**Baseline**	**Coal Measures**	**Borehole**	**30-100 m**	**Improved grassland**
45	**S08-01102**	**Baseline**	**Inverclyde Group**	**Borehole**	**30-100 m**	**Semi natural**
46	S08-01103	Baseline	Coal Measures	Borehole	30-100 m	Industrial/urban
47	S08-01104	Baseline	Coal Measures	Borehole	30-100 m	Semi natural
48	S08-01105	Baseline	Clackmannan Group	Borehole	30-100 m	Identified DPP
49	S08-01106	Baseline	Coal Measures	Borehole	unknown	Mixed cultivated
50	S08-01107	Baseline	Clackmannan Group	Borehole	30-100 m	Industrial/urban
51	**S08-01108**	**Baseline**	**Clackmannan Group**	**Borehole**	**30-100 m**	**Improved grassland**
52	S08-01109	Baseline	Coal Measures	Borehole	30-100 m	Identified DPP
53	**S08-01110**	**Baseline**	**Inverclyde Group**	**Borehole**	**unknown**	**Mixed cultivated**
54	S08-01111	Baseline	Clackmannan Group	Borehole	30-100 m	Identified DPP
55	S08-01112	Baseline	Clackmannan Group	Borehole	30-100 m	Identified DPP
56	**S08-01113**	**Baseline**	**Strathclyde Group**	**Borehole**	**>100 m**	**Recreational**
57	S08-01114	Baseline	Mine	Shaft	>100 m	Industrial/urban
58	S08-01115	Baseline	Mine	Shaft	>100 m	Industrial/urban
59	S08-01116	Baseline	Mine	Borehole	unknown	Arable
60	**S08-01117**	**Baseline**	**Clackmannan Group**	**Borehole**	**unknown**	**Semi natural**
61	S08-01118	Baseline	Clackmannan Group	Borehole	unknown	Semi natural
62	S08-01119	Baseline	Mine	Adit/Mine	unknown	Semi natural

[1] Orig NO_3 – Original Nitrate Project (Ball and MacDonald 2001).

[2] Springs – Scottish springs survey (Ball et al. 2006)

[3] SGMN – Scottish Groundwater Monitoring Network (MacDonald et al. 2005b)

[4] Irvine – small groundwater resource investigation (Ball and Graham 2006)

[5] DPP – Dairy, Pigs and Poultry

The eleven samples selected as representative examples of baseline conditions in the Carboniferous sedimentary aquifers of the Midland Valley are highlighted in bold.

The ID numbers in the left hand column are used to refer to the samples throughout the report. For sample locations see Figure 9.

Appendix 2 Summary statistics for chemical elements in groundwaters from individual Carboniferous aquifers in the Midland Valley

Table A2.1 Summary statistics for chemical elements in sampled groundwaters from the Coal Measures Group aquifer in the Midland Valley

Elem	Units	No.	No. cens	min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	10	0	9.9	10.3	10.6	10.9	12.3	14.6	14.9	15.1	
DO	mg/L	10	0	0.13	0.166	0.278	1.07	1.68	2.33	5.06	7.8	
SEC	µS/cm	10	0	274	472	666	950	1210	4520	18200	31800	
Ca	mg/L	10	0	3.4	12.6	41.9	58.4	74.3	321	981	1640	
Mg	mg/L	10	0	1.08	6.39	13.1	25.2	41.4	99.2	155	210	
Na	mg/L	10	0	10.4	11.9	31.8	93.8	133	769	3060	5360	
K	mg/L	10	0	1.43	2.15	3.14	9.19	12.6	28.9	60.6	92.2	
Cl	mg/L	10	0	12	14	14.8	21	42.7	1210	6350	11500	
SO_4	mg/L	10	0	4.98	7.18	9.4	23.6	51	89.1	148	206	
HCO_3	mg/L	8	0	251	285	413	466	518	600	668	736	
P	µg/L	10	3	<3			5	26			432	KM
DOC	mg/L	8	0	0.53	0.6	0.787	0.945	1.44	1.65	1.72	1.78	
F	mg/L	10	0	0.086	0.117	0.156	0.185	0.469	0.744	0.872	1	
Br	µg/L	10	0	56	71.3	84.2	110	218	12900	70000	127000	
I	µg/L	9	0	2.4	2.88	6.5	7.5	12.3	22.9	33.8	44.8	
Si	mg/L	10	0	3.78	3.89	4.87	5.68	6.54	7.28	8.94	10.6	
Ag	µg/L	10	7	<0.05	3E-05	0.0001	0.001	0.002	0.032	0.067	0.103	ROS
Al	µg/L	10	0	0.5	0.86	1.15	1.8	10.9̄	28.6	61.3	94	
As	µg/L	10	1	<0.05		0.12	0.31	0.8			10.8	KM
B	µg/L	10	0	21	32.7	102	140	302	354	445	536	
Ba	mg/L	10	0	0.0543	0.0882	0.151	0.255	0.541	2.83	11.5	20.1	
Be	µg/L	10	4	<0.05			0.003	0.011			0.289	KM
Cd	µg/L	10	1	<0.05	0.001	0.007	0.035	0.075			0.156	KM
Ce	µg/L	10	0	0.003	0.0084	0.0105	0.0125	0.019	0.192	0.302	0.413	
Co	µg/L	10	0	0.02	0.0506	0.0955	0.56	1.71̄	2.54	4.43	6.32	
Cr	µg/L	10	5	<0.2				0.5			0.8	KM
Cs	µg/L	10	0	0.032	0.0653	0.078	0.105	0.337	0.652	1.43	2.21	
Cu	µg/L	10	3	<0.5			1.1	2.1			5.6	KM
Dy	µg/L	10	1	<0.01	0.003	0.005	0.007	0.013			0.241	KM
Er	µg/L	10	0	0.002	0.0047	0.005	0.006	0.01	0.031	0.109	0.188	
Eu	µg/L	10	0	0.01	0.01	0.0155	0.0265	0.072	0.437	1.99	3.54	
Fe	µg/L	10	0	4	29.2	134	1220	4830	24500	30100	35600	
Ga	µg/L	10	2	<0.05		0.006	0.009	0.029			0.176	KM
Gd	µg/L	10	0	0.002	0.0038	0.004	0.006	0.011	0.035	0.114	0.192	
Hf	µg/L	10	4	<0.02			0.01	0.01̄			0.03	KM
Ho	µg/L	10	1	<0.01	0.001	0.001	0.002	0.003			0.056	KM
La	µg/L	10	0	0.006	0.006	0.0083	0.015	0.066	0.141	0.194	0.247	
Li	µg/L	10	0	6.12	6.95	8.51	11.6	22.8̄	47.1	115	182	
Lu	µg/L	10	4	<0.01			0.002	0.004			0.122	KM
Mn	µg/L	10	0	1.24	2.9	23.6	190	435	620	724	829	

Elem	Units	No.	No. cens	min	10%	25%	50%	75%	90%	95%	max	method[1]
Mo	µg/L	10	2	<0.2		0.3	0.3	0.5			1	KM
Nd	µg/L	10	0	0.004	0.0085	0.0093	0.012	0.069	0.147	0.256	0.365	
Ni	µg/L	10	3	<0.5			0.8	3.2			10.2	KM
Pb	µg/L	10	1	<0.1	0.03	0.03	0.06	0.23			13.3	KM
Pr	µg/L	10	1	<0.01	0.001	0.002	0.003	0.004			0.067	KM
Rb	µg/L	10	0	2.37	3.39	3.78	10.7	12.6	35.5	90.3	145	
Sb	µg/L	10	1	<0.05	0.01	0.01	0.02	0.04			0.25	KM
Sm	µg/L	10	1	<0.02	0.003	0.004	0.008	0.022			0.186	KM
Sn	µg/L	10	7	<0.08	0.0008	0.0024	0.004	0.077	0.172	0.451	0.73	ROS
Sr	mg/L	10	0	0.091	0.119	0.433	0.964	2.61	11.1	43	74.9	
Ta	µg/L	10	6	<0.02	0.0035	0.0047	0.006	0.01	0.011	0.016	0.02	ROS
Tb	µg/L	10	6	<0.01	3E-05	9E-05	0.0002	0.002	0.005	0.020	0.034	ROS
Th	µg/L	10	2	<0.05		0.005	0.009	0.02			0.979	KM
Ti	µg/L	10	1	<10	0.01	0.03	0.05	0.27	0.67	0.67	0.67	KM
Tl	µg/L	10	7	<0.01	0.0005	0.0008	0.001	0.004	0.008	0.017	0.026	ROS
Tm	µg/L	10	6	<0.01	4E-05	0.0001	0.0004	0.002	0.016	0.022	0.029	ROS
U	µg/L	10	0	0.003	0.0048	0.114	0.226	0.443	4.57	4.79	5.01	
V	µg/L	10	1	<0.2	0.02	0.04	0.14	0.38			2.27	KM
W	µg/L	10	8	<0.04							0.184	ROS
Y	µg/L	10	2	<0.05		0.07	0.08	0.19			1.09	KM
Yb	µg/L	10	0	0.004	0.0049	0.005	0.010	0.015	0.207	0.263	0.318	
Zn	µg/L	10	0	2.2	4.18	4.78	10.1	12.4	16.4	21.8	27.2	
Zr	µg/L	10	0	0.002	0.0038	0.0437	0.062	0.118	0.179	0.285	0.392	

[1] Statistical method (for more details see Section 4.1.1). Where >80% of samples were non-detects, ranges only are quoted.

KM: Kaplan-Meier, used when <50% of the samples in the dataset are censored

ROS: Regression on Order Statistics, used when >50% but <80% of the samples in the dataset are censored

All the NO_2-N values were below detection limit of 0.0009 mg/L; all but one of the NO_3-N values were below the detection limit of 0.05 mg/L: the remaining value was 7.29 mg/L.

Table A2.2 Summary statistics for chemical elements in sampled groundwaters from the Clackmannan Group aquifer in the Midland Valley

Elem	Units	No.	No. cens	min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	21	0	8.4	8.6	9.2	10.3	10.8	11.3	11.8	13.7	
DO	mg/L	19	1	<0.11	0.2	0.44	1.2	2.99	5.05		5.51	KM
SEC	µS/cm	21	0	137	310	357	596	774	1130	1430	4560	
Ca	mg/L	21	0	7.26	28.8	35.1	54.5	94.2	123	129	290	
Mg	mg/L	21	0	3.11	7.86	12.8	17.5	31.3	36.4	42.5	96.2	
Na	mg/L	21	0	6.2	8.2	11.6	15.5	33.2	134	182	461	
K	mg/L	21	0	0.64	1.49	2.41	3.08	4.41	10.3	11.6	26.8	
Cl	mg/L	21	0	5.14	7.22	11.8	20.7	29.8	64.7	117	1230	
SO_4	mg/L	21	0	3.82	9	19.6	48.5	83.2	107	115	244	
HCO_3	mg/L	21	0	7	94	181	265	366	508	606	734	
P	µg/L	21	9	<20			7	24	103	105	167	KM
DOC	mg/L	15	0	0.45	0.748	1.08	1.22	2.04	29.9	54.2	70.8	
F	mg/L	21	0	0.033	0.069	0.108	0.15	0.246	0.312	0.338	0.793	
Br	µg/L	21	1	<100	43	63	97	123	215	8040	9060	KM
I	µg/L	17	3	<2		3	5	6.8	22.2		74.3	KM
Si	mg/L	21	0	1.95	3.07	3.61	4.65	7.11	8.23	10.2	12.9	
Al	µg/L	21	0	0.2	1.2	1.6	4	8.2	19	28.7	76.9	
As	µg/L	21	12	<0.5	0.0324	0.0535	0.111	0.17	0.25	0.25	1	ROS
B	µg/L	21	1	<20	14	25	63	168	200	299	371	KM
Ba	mg/L	21	0	0.031	0.044	0.07	0.121	0.259	0.644	2.3	5.64	
Cd	µg/L	21	7	<0.05	0.005	0.008	0.023	0.042	0.089	0.094	0.135	KM
Ce	µg/L	21	3	<0.05	0.004	0.009	0.011	0.022	0.071	0.864	1.31	KM
Co	µg/L	21	2	<0.05	0.008	0.024	0.09	0.455	13.1	19.7	25.8	KM
Cr	µg/L	21	15	<0.5	0.0763	0.113	0.169	0.204	0.282	0.8	1.1	ROS
Cs	µg/L	21	4	<0.05		0.027	0.042	0.069	0.176	0.255	0.26	KM
Cu	µg/L	21	7	<0.5	0.44	0.44	0.7	0.9	1.2	1.5	20.9	KM
Dy	µg/L	21	9	<0.05	0.002	0.002	0.006	0.008	0.019	0.078	0.116	KM
Eu	µg/L	21	3	<0.05	0.005	0.007	0.01	0.04	0.059	0.067	0.245	KM
Fe	µg/L	21	0	11	26	32	322	1500	3940	6420	6520	
Gd	µg/L	21	6	<0.05	0.001	0.003	0.007	0.01	0.06	0.127	0.145	KM
Hf	µg/L	21	14	<0.05	0.00511	0.00616	0.00813	0.01	0.0102	0.0119	0.02	ROS
Hg	µg/L	7	4	<0.1	0.0049	0.0105	0.0286	0.15	0.32	0.41	0.5	ROS
Ho	µg/L	21	12	<0.05	0.0001	0.00027	0.001	0.002	0.007	0.016	0.025	ROS
La	µg/L	21	3	<0.05	0.008	0.01	0.02	0.028	0.05	0.373	0.768	KM
Li	µg/L	21	0	1.4	3.5	4.9	7	12.7	24	25.3	27.4	
Lu	µg/L	21	15	<0.05	0.0004	0.0007	0.00132	0.00276	0.0052	0.0065	0.011	ROS
Mn	µg/L	21	0	2.13	7.27	27.7	103	329	465	563	1950	
Mo	µg/L	21	7	<0.2		0.1	0.2	0.3	0.9	0.9	1.42	KM
Nd	µg/L	21	5	<0.05	0.005	0.005	0.015	0.03	0.044	0.606	0.911	KM

Elem	Units	No.	No. cens	min	10%	25%	50%	75%	90%	95%	max	method[1]
Ni	µg/L	21	9	<0.5	0.14	0.14	0.69	2.1	20.9	32.1	43.1	KM
Pb	µg/L	21	5	<0.1	0.01	0.02	0.05	0.1	0.13	0.13	0.2	KM
Pr	µg/L	21	9	<0.05	0.001	0.002	0.004	0.005	0.01	0.131	0.21	KM
Rb	µg/L	21	0	0.85	1.05	1.66	4.35	5.45	10.4	19.8	30.4	
Re	µg/L	7	4	<0.01	0.002	0.00291	0.00489	0.01	0.014	0.017	0.02	ROS
Sb	µg/L	21	9	<0.05	0.01	0.01	0.01	0.03	0.04	0.04	0.12	KM
Se	µg/L	9	4	<0.5	0.09	0.09	0.37	0.5			2.7	KM
Sm	µg/L	21	8	<0.05	0.004	0.005	0.006	0.013	0.05	0.129	0.151	KM
Sn	µg/L	21	11	<0.08	0.00995	0.0278	0.0481	0.55	0.63	0.85	1.37	ROS
Sr	mg/L	21	0	0.039	0.124	0.173	0.565	0.812	1.71	4.42	8.22	
Tb	µg/L	21	16	<0.05	4.43E-05	0.000128	0.000426	0.002	0.0058	0.0173	0.02	ROS
Th	µg/L	21	11	<0.05	0.00126	0.00169	0.00228	0.00522	0.0088	0.0121	0.016	ROS
Tl	µg/L	21	16	<0.05	0.000341	0.000653	0.00176	0.00375	0.019	0.021	0.119	ROS
TON	mg/L	7	5	<1	0.0412	0.0605	0.0605	1.21	4.4	6.05	7.7	ROS
U	µg/L	21	2	<0.05	0.016	0.02	0.04	0.679	1.5	1.88	2.04	KM
V	µg/L	21	4	<0.2	0.02	0.03	0.07	0.13	0.2	0.3	0.4	KM
Y	µg/L	21	6	<0.05	0.03	0.03	0.04	0.07	0.22	0.41	0.8	KM
Yb	µg/L	21	9	<0.05	0.002	0.003	0.005	0.009	0.028	0.028	0.067	KM
Zn	µg/L	21	0	0.8	1.3	2.13	3.7	11.4	76.2	170	204	
Zr	µg/L	21	8	<0.05		0.007	0.02	0.06	0.08	0.088	0.127	KM

[1] Statistical method (for more details see Section 4.1.1). Where >80% of samples were non-detects, ranges only are quoted.

KM: Kaplan-Meier, used when <50% but <80% of the samples in the dataset are censored

ROS: Regression on Order Statistics, used when >50% of the samples in the dataset are censored

TON: Total Organic Nitrogen

Table A2.3 Summary statistics for chemical elements in sampled groundwaters from the Strathclyde Group aquifer in the Midland Valley

Elem	Units	No	No. cens	Min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	15	0	7.1	7.43	8	9.5	11.9	13.8	15.5	17.9	
DO	mg/L	8	0	0.8	1.33	1.87	2.75	4.35	7.34	8.77	10.2	
SEC	µS/cm	16	0	334	445	632	744	1060	1260	1630	2400	
Ca	mg/L	16	0	28.3	37.2	49.6	57.6	74.4	116	157	269	
Mg	mg/L	16	0	4.51	10.4	16.9	29	34.7	51.8	55.6	56.1	
Na	mg/L	16	0	9.9	14.5	28.8	44.9	94.7	188	213	245	
K	mg/L	16	0	1.2	2.16	4.08	8.29	8.88	10.7	11.3	12.4	
Cl	mg/L	16	0	13.6	26.5	37.2	48.5	108	154	310	692	
SO_4	mg/L	16	1	<0.1	0.15	25.1	34.2	45.8	170		179	KM
HCO_3	mg/L	16	0	132	179	260	315	384	428	459	480	
P	µg/L	16	10	<20	1.57	2.71	6.29	20.5	36.5	51	60	ROS
DOC	mg/L	5	0	1.05	1.09	1.14	1.25	1.36	1.4	1.41	1.42	
F	mg/L	16	0	0.085	0.102	0.191	0.32	0.375	0.565	0.777	1.04	
Br	µg/L	16	0	49	104	146	208	706	1180	3410	9100	
I	µg/L	13	0	3.6	4.36	5	9.4	16	67.6	99.1	139	
Si	mg/L	16	0	3.12	3.45	3.91	4.8	5.82	7.39	8.83	9.5	
Ag	µg/L	16	12	<0.05	3E-05	0.0001	0.0005	0.0094	0.18	0.352	0.69	ROS
Al	µg/L	16	0	1.6	1.95	2	3	5.25	8	12	18	
As	µg/L	16	8	<0.5			0.22	0.5	5.4		5.6	KM
B	µg/L	16	0	22	37.5	88.2	138	262	288	313	339	
Ba	mg/L	16	0	0.019	0.042	0.0765	0.228	0.406	1.32	2.14	2.41	
Cd	µg/L	16	10	<0.05	0.007	0.0114	0.02	0.0347	0.0613	0.122	0.29	ROS
Ce	µg/L	16	1	<0.01	0.003	0.007	0.01	0.01	0.02	NA	0.03	KM
Co	µg/L	16	0	0.02	0.0325	0.05	0.12	0.302	0.555	0.585	0.63	
Cs	µg/L	16	1	<0.01	0.005	0.03	0.04	0.1	0.12		0.32	KM
Cu	µg/L	16	1	<0.5	0.3	0.5	1.5	3.1	6.1		77	KM
Dy	µg/L	16	10	<0.01	0.0011	0.0017	0.0023	0.0038	0.0059	0.007	0.01	ROS
Eu	µg/L	16	1	<0.01	0.002	0.01	0.039	0.043	0.21		0.257	KM
Fe	µg/L	16	1	<10	4	6	79	650	1690		3930	KM
Ga	µg/L	16	12	<0.05	0.0124	0.0156	0.0194	0.0268	0.0327	0.0416	0.06	ROS
Gd	µg/L	16	4	<0.01	0.001	0.002	0.005	0.01	0.01		0.04	KM
Hg	µg/L	11	3	<0.1			0.8	1	1.2		1.4	KM
La	µg/L	16	3	<0.01	0.004	0.004	0.01	0.017	0.029		0.05	KM
Li	µg/L	16	0	3.54	8.85	10.6	11.8	18.7	51	59	63.2	
Mn	µg/L	16	0	0.56	3.62	24.6	41.8	66.6	147	232	303	
Mo	µg/L	16	4	<0.2		0.1	0.2	0.7	1.6		4.4	KM
Nb	µg/L	16	10	<0.02	0.0013	0.0022	0.0051	0.01	0.02	0.035	0.05	ROS
Nd	µg/L	16	3	<0.01	0.004	0.006	0.01	0.01			0.02	KM
Ni	µg/L	16	7	<0.5			0.4	1	3.3		5.3	KM

Elem	Units	No	No. cens	Min	10%	25%	50%	75%	90%	95%	max	method[1]
Pb	µg/L	16	6	<0.1	0.03	0.05	0.07	0.12	0.31		0.4	KM
Pr	µg/L	16	10	<0.01	0.0009	0.0011	0.0019	0.0028	0.0038	0.0058	0.01	ROS
Rb	µg/L	16	0	0.47	3.22	4.81	7.81	8.86	11.1	11.8	13.7	
Re	µg/L	11	7	<0.01	0.0002	0.0006	0.0024	0.015	0.05	0.07	0.09	ROS
Rh	µg/L	11	6	<0.01	0.0008	0.0017	0.004	0.01	0.01	0.03	0.05	ROS
Sb	µg/L	16	10	<0.05	0.0089	0.0114	0.0193	0.0342	0.05	0.0525	0.06	ROS
Se	µg/L	7	0	0.9	0.9	0.95	1.4	2.2	3.42	3.81	4.2	
Sm	µg/L	16	10	<0.02	0.0017	0.0033	0.0057	0.0094	0.0164	0.0185	0.02	ROS
Sn	µg/L	16	4	<0.06			0.26	0.38	0.72		0.97	KM
Sr	mg/L	16	0	0.184	0.236	0.494	0.591	1.02	1.61	3.46	7.68	
Ti	µg/L	16	10	<10	0.0076	0.0176	0.0423	0.185	0.531	3.8	13	ROS
Tl	µg/L	16	12	<0.01	0.0002	0.0005	0.0009	0.0025	0.008	0.01	0.01	ROS
TON	mg/L	11	7	<1	0.0255	0.0538	0.102	0.85	2.7	3.5	4.3	ROS
U	µg/L	16	1	<0.02	0.009	0.02	0.112	0.36	3.66		5.71	KM
V	µg/L	16	2	<0.2	0.03	0.05	0.4	0.8	2.57		2.8	KM
Y	µg/L	16	3	<0.05	0.01	0.02	0.04	0.06	0.07		0.11	KM
Yb	µg/L	16	10	<0.01	0.0013	0.0022	0.0036	0.0059	0.0085	0.0105	0.012	ROS
Zn	µg/L	16	0	2.5	4.35	10.5	17.9	62	136	175	212	
Zr	µg/L	16	3	<0.02	0.009	0.017	0.03	0.06	0.11		0.31	KM

[1] Statistical method (for more details see Section 4.1.1). Where >80% of samples were non-detects, ranges only are quoted.

KM: Kaplan-Meier, used when <50% but <80% of the samples in the dataset are censored

ROS: Regression on Order Statistics, used when >50% of the samples in the dataset are censored

TON: Total Organic Nitrogen

Table A2.4 Summary statistics for chemical elements in sampled groundwaters from the Inverclyde Group aquifer in the Midland Valley

Elem	Units	No	No. cens	min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	9	0	7.9	7.98	8.4	9.2	11	13	13.4	13.8	
DO	mg/L	8	0	0.16	1.34	2.18	3.38	8.04	9.76	10.3	10.8	
SEC	µS/cm	9	0	177	307	409	510	695	851	916	981	
Ca	mg/L	9	0	38.4	40.4	54.4	66	70.6	72	74.5	77.1	
Mg	mg/L	9	0	6.16	9.47	11.6	19	27.2	36.8	42.5	48.2	
Na	mg/L	9	0	5.59	6	7.51	8.5	20.1	60.9	82.4	104	
K	mg/L	9	0	1.16	1.16	1.23	1.76	5.09	5.95	7.45	8.95	
Cl	mg/L	9	0	5.74	5.93	6.88	12.8	20.5	35.8	62.1	88.5	
SO_4	mg/L	9	0	0.93	1.68	4.65	13	28.7	65.8	96.9	128	
HCO_3	mg/L	9	0	188	213	246	256	313	357	429	500	
P	µg/L	9	4	<20			20	31			53	KM
DOC	mg/L	4	0	0.56	0.56	0.56	0.88	1.35	1.62	1.71	1.8	
F	mg/L	8	0	0.041	0.0417	0.048	0.0515	0.149	0.288	0.356	0.425	
Br	µg/L	9	0	32	34.4	62	133	355	421	478	536	
I	µg/L	7	0	3.4	3.4	4.35	5.7	6.5	10.3	12.7	15.2	
Si	mg/L	9	0	3.93	4.48	4.9	5.43	5.71	6.6	6.77	6.95	
Al	µg/L	9	0	0.4	0.88	1.5	2.5	4	7.2	11.6	16	
As	µg/L	9	1	<0.5	0.07	0.1	0.8	1.22			2.7	KM
B	µg/L	9	2	<20	6	12	29	160			382	KM
Ba	mg/L	9	0	0.05	0.153	0.199	0.362	0.396	1.33	2.33	3.32	
Cd	µg/L	9	3	<0.05	0.016	0.018	0.025	0.08			0.12	KM
Ce	µg/L	9	2	<0.01	0.002	0.004	0.01	0.01			0.14	KM
Co	µg/L	9	0	0.012	0.0128	0.06	0.12	0.38	3.45	7.48	11.5	
Cr	µg/L	9	4	<0.5			0.5	0.7			0.9	KM
Cs	µg/L	9	1	<0.01		0.01	0.03	0.076			0.353	KM
Cu	µg/L	9	0	0.5	0.9	1.2	2	3.7	11.3	25	38.8	
Dy	µg/L	9	2	<0.01	0.003	0.004	0.006	0.01			0.071	KM
Eu	µg/L	9	0	0.008	0.0184	0.024	0.05	0.2	0.324	0.572	0.82	
Fe	µg/L	9	1	<10	2	2	18	205			540	KM
Gd	µg/L	9	4	<0.01	0.002	0.002	0.002	0.004			0.04	KM
Ge	µg/L	5	4	<0.05							0.25	ROS
Hg	µg/L	5	4	<0.1							0.6	ROS
Ho	µg/L	9	6	<0.01	0.0001	0.0001	0.0009	0.002	0.0069	0.016	0.025	ROS
La	µg/L	9	0	0.006	0.0092	0.01	0.015	0.03	0.074	0.082	0.09	
Li	µg/L	9	0	1.24	2.49	2.8	5.6	18.5	29.6	41.5	53.4	
Lu	µg/L	9	7	<0.01	4E-05	0.0001	0.0003	0.003	0.0114	0.028	0.045	ROS
Mn	µg/L	9	0	0.45	2.28	2.9	6.18	71.3	119	169	220	
Mo	µg/L	9	3	<0.2		0.1	0.1	0.6			5	KM
Nb	µg/L	9	7	<0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS

Nd	µg/L	9	2	<0.01	0.006	0.007	0.01	0.023			0.1	KM
Ni	µg/L	9	5	<0.5	0.0059	0.0099	0.0795	1.5	11.7	26	40.3	ROS
Pb	µg/L	9	2	<0.1	0.03	0.03	0.1	0.26			7.02	KM
Pr	µg/L	9	4	<0.01	0.002	0.002	0.002	0.004			0.02	KM
Rb	µg/L	9	0	0.95	1.02	1.41	1.65	3.1	5.61	9.56	13.5	
Rh	µg/L	5	2	<0.01			0.01	0.01			0.02	KM
Sb	µg/L	9	5	<0.05	0.0166	0.02	0.0249	0.034	0.0644	0.097	0.13	ROS
Se	µg/L	5	1	<0.5		0.8	1.1	2.4			2.6	KM
Sm	µg/L	9	3	<0.02	0.002	0.002	0.007	0.009			0.04	KM
Sn	µg/L	9	4	<0.08			0.1	0.21			0.65	KM
Sr	mg/L	9	0	0.079	0.0982	0.18	0.292	2.33	3.84	5.15	6.46	
Tl	µg/L	9	7	<0.01	0.0005	0.0005	0.0025	0.0051	0.0282	0.041	0.053	ROS
TON	mg/L	5	3	<1	0.194	0.194	0.194	0.211	0.22	0.224	0.227	ROS
U	µg/L	9	0	0.07	0.166	0.257	0.84	2.81	3.79	4.26	4.74	
V	µg/L	9	2	<0.2	0.04	0.04	0.4	0.9			1.7	KM
Y	µg/L	9	1	<0.05	0.02	0.03	0.09	0.11			0.58	KM
Yb	µg/L	9	3	<0.01	0.003	0.003	0.003	0.01			0.234	KM
Zn	µg/L	9	0	1.7	2.9	3.3	4.9	7.3	15.9	25.4	34.8	
Zr	µg/L	9	5	<0.02	0.0008	0.0016	0.0033	0.018	0.0308	0.032	0.034	ROS

[1] Statistical method (for more details see Section 4.1.1). Where >80% of samples were non<detects, ranges only are quoted.

KM: Kaplan-Meier, used when <50% but <80% of the samples in the dataset are censored

ROS: Regression on Order Statistics, used when >50% of the samples in the dataset are censored

TON: Total Organic Nitrogen

Table A2.5 Summary statistics for chemical elements in sampled 'Mine' waters from Carboniferous aquifers in the Midland Valley

Elem	Units	No	No. cens	min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	6	0	9.8	10.6	11.4	12.1	14	16.9	18	19.2	
DO	mg/L	6	3	<0.1				3.12			12.8	KM
SEC	µS/cm	6	0	740	1020	1340	1830	4340	7920	9360	10800	
Ca	mg/L	6	0	66.4	88.2	115	142	234	302	321	341	
Mg	mg/L	6	0	36.2	42.9	61	108	193	327	382	437	
Na	mg/L	6	0	16.3	21.1	35.1	114	696	1120	1240	1360	
K	mg/L	6	0	8.07	8.11	9.8	19.9	29.6	42.2	47.7	53.3	
Cl	mg/L	6	0	13.8	15.1	23.4	119	1050	2050	2410	2770	
SO_4	mg/L	6	0	103	130	192	456	1190	1740	1920	2100	
HCO_3	mg/L	6	0	346	373	404	444	511	545	556	566	
P	µg/L	4	0	8.01	8.95	10.4	15.9	21.3	22.6	23.1	23.5	
DOC	mg/L	6	0	1.28	1.41	1.57	1.69	1.75	2.1	2.28	2.45	
F	mg/L	6	1	<0.05		0.13	0.171	0.214			0.315	KM
Br	µg/L	6	1	<100		120	243	5140			8800	KM
I	µg/L	6	0	2.3	3.55	5.02	14.1	24.8	38.9	45.6	52.2	
Si	mg/L	6	0	4.29	4.48	4.75	5.54	6.52	7.21	7.49	7.76	
Al	µg/L	6	0	7.3	7.85	8.8	13	22.8	43.7	53	62.4	
As	µg/L	4	0	0.2	0.275	0.388	0.46	0.562	0.729	0.784	0.84	
B	µg/L	6	0	46.6	96.3	151	228	455	662	738	814	
Ba	mg/L	6	0	0.016	0.026	0.036	0.050	0.088	0.235	0.304	0.373	
Cd	µg/L	4	2	<0.05							0.601	KM
Ce	µg/L	4	2	<0.05							5.29	KM
Co	µg/L	4	0	1.1	2.66	5	31.6	61.3	69.5	72.2	74.9	
Cr	µg/L	4	1	<0.05			0.16				0.24	KM
Cs	µg/L	4	0	0.214	0.222	0.234	0.242	0.275	0.33	0.349	0.367	
Cu	µg/L	4	0	0.43	0.457	0.497	0.63	0.75	0.768	0.774	0.78	
Dy	µg/L	4	3	<0.05	0.818	0.818	0.818	0.818	0.818	0.818	0.818	ROS
Eu	µg/L	4	3	<0.05	0.185	0.185	0.185	0.185	0.185	0.185	0.185	ROS
Fe	µg/L	6	0	435	528	968	3280	37600	92600	115000	137000	
Gd	µg/L	4	3	<0.05	0.918	0.918	0.918	0.918	0.918	0.918	0.918	ROS
Ho	µg/L	4	3	<0.05	0.169	0.169	0.169	0.169	0.169	0.169	0.169	ROS
La	µg/L	4	3	<0.05	2.15	2.15	2.15	2.15	2.15	2.15	2.15	ROS
Li	µg/L	6	0	11.8	29.2	46.8	48.2	65.6	88.2	96.7	105	
Mn	µg/L	6	0	196	286	494	1970	3230	5700	6910	8120	
Mo	µg/L	4	0	0.11	0.149	0.207	0.24	0.265	0.31	0.325	0.34	
Nd	µg/L	4	2	<0.05							2.87	KM
Ni	µg/L	6	0	1.8	3.4	5.95	10.2	70.8	92.7	93.8	94.9	
Pb	µg/L	4	2	<0.05							0.09	KM

Elem	Units	No	No. cens	min	10%	25%	50%	75%	90%	95%	max	method[1]
Pr	µg/L	4	3	<0.05	0.664	0.664	0.664	0.664	0.664	0.664	0.664	ROS
Rb	µg/L	4	0	13.6	17.7	23.9	36	47.5	52.4	54	55.6	
Se	µg/L	4	1	<0.05			0.06				0.45	KM
Sm	µg/L	4	3	<0.05	0.576	0.576	0.576	0.576	0.576	0.576	0.576	ROS
Sn	µg/L	4	3	<0.05	0.19	0.19	0.19	0.19	0.19	0.19	0.19	ROS
Sr	mg/L	6	0	0.51	0.765	1.14	2.01	2.67	3.01	3.16	3.31	
Tb	µg/L	4	3	<0.05	0.141	0.141	0.141	0.141	0.141	0.141	0.141	ROS
U	µg/L	4	0	0.312	0.395	0.52	0.78	1.32	1.96	2.17	2.38	
V	µg/L	6	3	<2			0.07	0.13	0.23	0.23	0.23	KM
Y	µg/L	6	2	<0.3	0.09	0.09	0.11	0.2			5.55	KM
Yb	µg/L	4	3	<0.05	0.25	0.25	0.25	0.25	0.25	0.25	0.25	ROS
Zn	µg/L	6	0	3.41	4.14	6.91	15.3	20	24.8	26.8	28.9	
Zr	µg/L	4	3	<0.05	0.07	0.07	0.07	0.07	0.07	0.07	0.07	ROS

[1] Statistical method (for more details see Section 4.1.1). Where >80% of samples were non-detects, ranges only are quoted.

KM: Kaplan-Meier, used when <50% but <80% of the samples in the dataset are censored

ROS: Regression on Order Statistics, used when >50% of the samples in the dataset are censored

TON: Total Organic Nitrogen